Supplementary Information for: Wetting dynamics under periodic switching on different scales: Characterization and mechanisms

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I. SNAPSHOTS

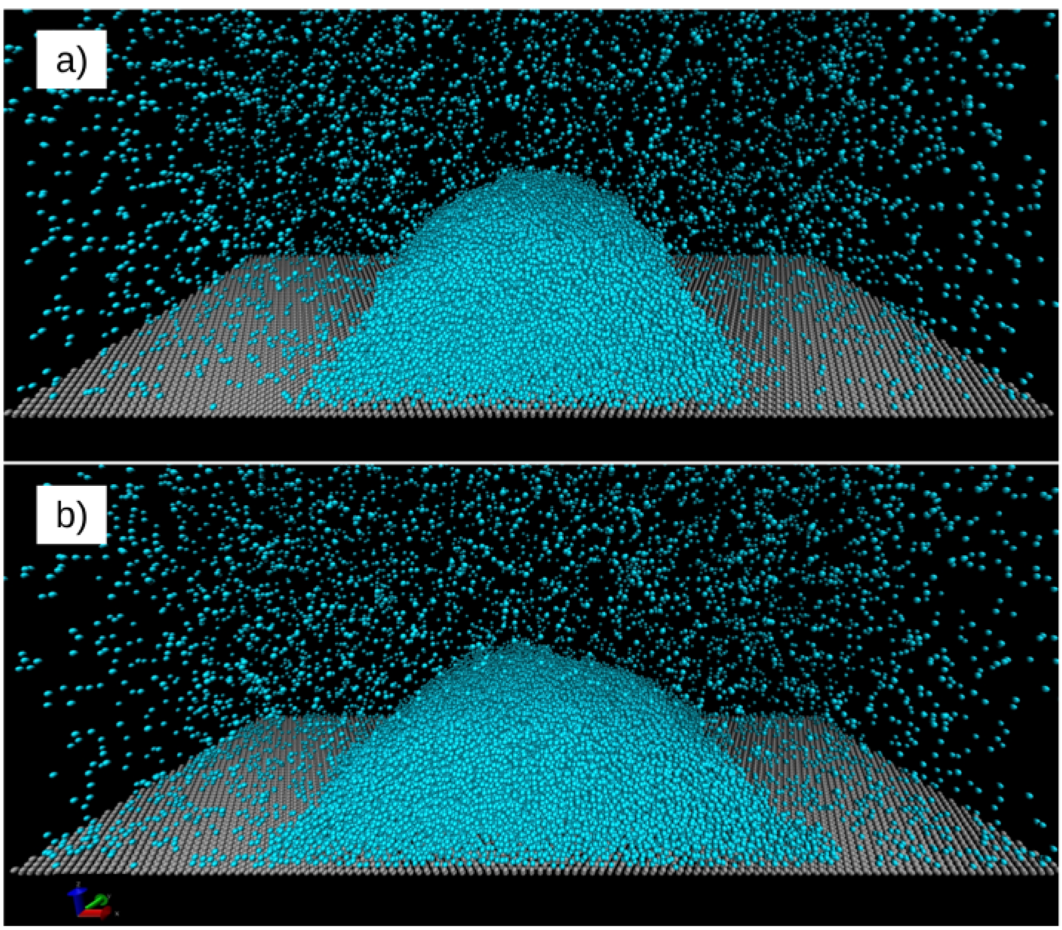

FIG. 1: Snapshots from the MD simulation of a droplet for switching between $\varepsilon_w = 0.632$ and $\varepsilon_w = 0.762$ with a switching frequency of $20 \cdot 10^4$ MD steps at MD steps of a) 0 and b) $10 \cdot 10^4$.

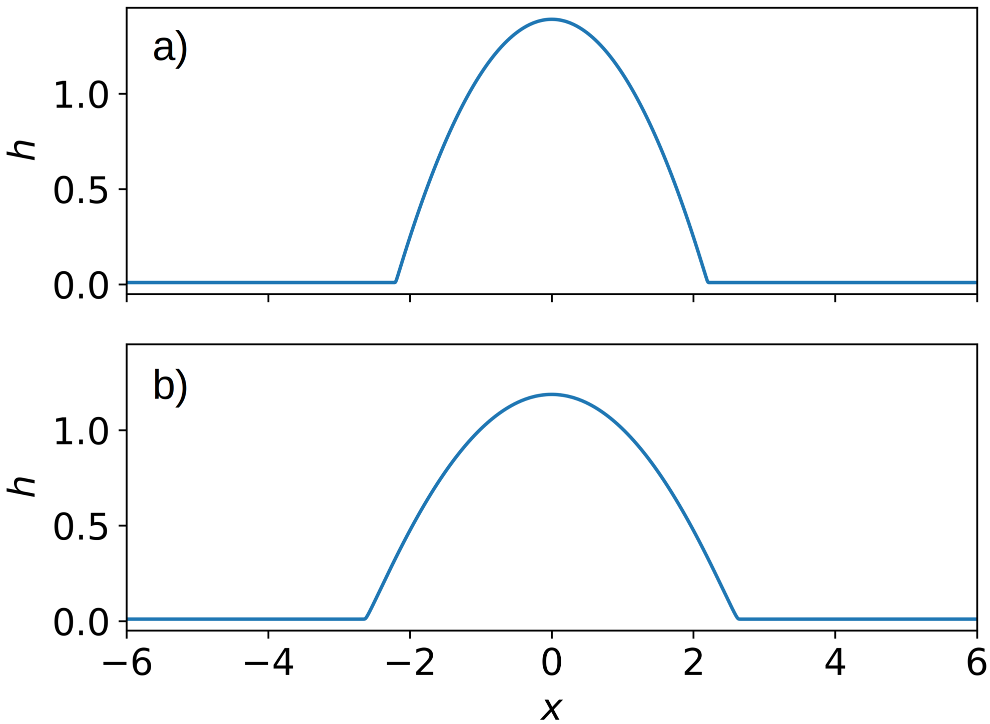

FIG. 2: Snapshots from the TF simulation of a droplet for switching between $\varepsilon_w = 0.632$ and $\varepsilon_w = 0.762$ with a switching frequency corresponding to $20 \cdot 10^4$ MD steps at corresponding MD steps of a) 0 and b) $10 \cdot 10^4$.

II. CALCULATION OF THE CONTACT ANGLE FROM RFWHM

For a spherical cap shaped droplet one has

$$r^2 = \left(\frac{\sigma}{2}\right)^2 + \left(r - \frac{h}{2}\right)^2 \tag{1}$$

where h is the height, r the radius of the droplet, and σ the width at half height. Therefore, the radius r can be expressed as

$$r = \frac{1}{4h}(\sigma^2 + h^2). \tag{2}$$

Further, basic trigonometry yields

$$\cos(\theta) = 1 - \frac{h}{r} \tag{3}$$

with the contact angle θ. By plugging Eq. (2) into Eq. (3) we get

$$\cos(\theta) = 1 - \frac{h}{\frac{1}{4h}(\sigma^2 + h^2)} \tag{4}$$

and finally we obtain

$$\cos(\theta) = 1 - \frac{4}{\frac{1}{\mathrm{rFWHM}^2} + 1}. \tag{5}$$

with the definition of the relative full width at half maximum rFWHM$= h/\sigma$.

III. REFORMULATION OF MKT EQUATION

The relation between the half chord length r and the half of the central angle θ of a circular segment is given by

$$r = \sqrt{2A}\frac{\sin(\theta)}{\sqrt{(2\theta - \sin(2\theta))}} = \sqrt{2A}f(\theta) \tag{6}$$

where A is the area of the circular segment. Here, we r is the radius of a droplet on a surface and θ is the contact angle. Then we can write

$$v_{cl} = \frac{dr}{dt} = \sqrt{2A}\frac{df}{d\theta}\frac{d\theta}{dt} = -\sqrt{2A}\frac{df}{d\theta}\frac{1}{sin(\theta)}\frac{d\cos(\theta)}{dt} \tag{7}$$

where

$$g(\theta) = \frac{df}{dt} = \frac{\cos(\theta)}{\sqrt{2\theta - \sin(2\theta)}} - \frac{\sin(\theta)(1 - \cos(2\theta))}{\sqrt{2\theta - \sin(2\theta)}^3}. \tag{8}$$

The MKT relation reads

$$v = k_0(\cos(\theta_{eq}) - \cos(\theta)) \tag{9}$$

with $k_0 = \frac{\gamma}{\zeta}$ and can thus be rewritten as

$$\frac{d}{dt}\cos(\theta) = -k_1\frac{\sin(\theta)}{g(\theta)}(\cos(\theta_{eq}) - \cos(\theta)) \tag{10}$$

with $k_1 = \frac{k_0}{\sqrt{2A}}$. As can be seen in Fig. 3 $\frac{-\sin(\theta)}{g(\theta)}$ can be approximated as $3(1 - \cos(\theta))$. Thus, Eq. (10) can be rewritten for intermediate changes in contact angles as

$$\frac{d}{dt}\cos(\theta) = k_2(1 - \cos(\theta))(\cos(\theta_{eq}) - \cos(\theta)) \tag{11}$$

and for small changes as

$$\frac{d}{dt}\cos(\theta) = k_3(\cos(\theta_{eq}) - \cos(\theta)) \tag{12}$$

where $k_3 = k_2(1 - \cos(\theta_{eq}))$ since $\cos(\theta)$ can be substituted by the constant $\cos(\theta_{eq})$. In Fig. 4 and 5 the two approximations and the solution from Eq. (10) are plotted for a single switching event and periodic switching.

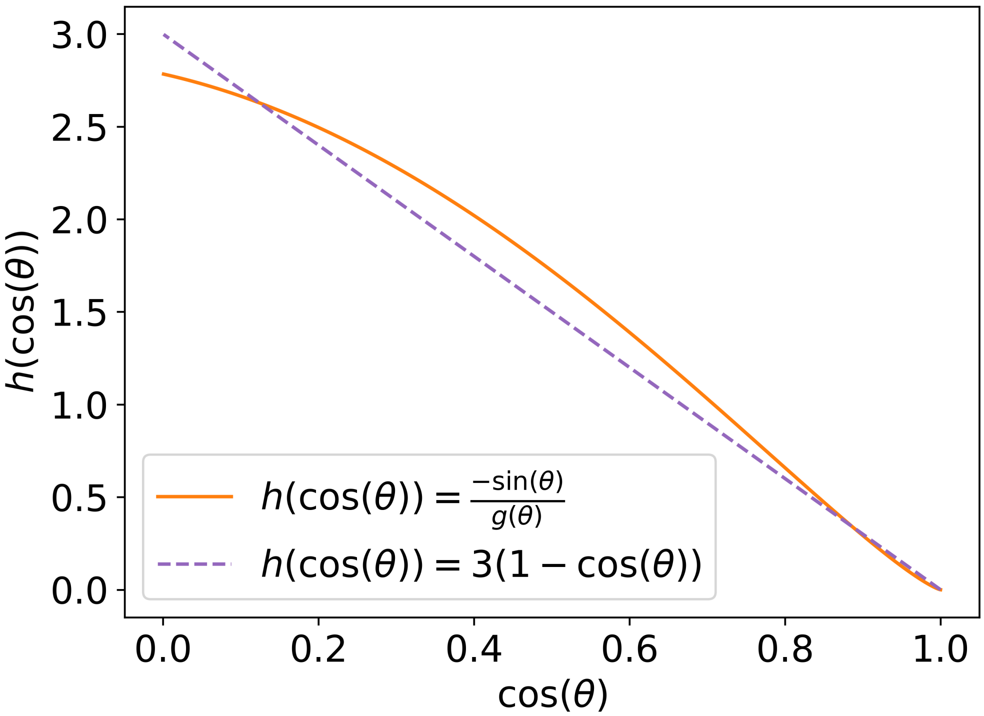

FIG. 3: $\frac{-\sin(\theta)}{g(\theta)}$ in comparison with $3(1-\cos(\theta))$ plotted versus $\cos(\theta)$.

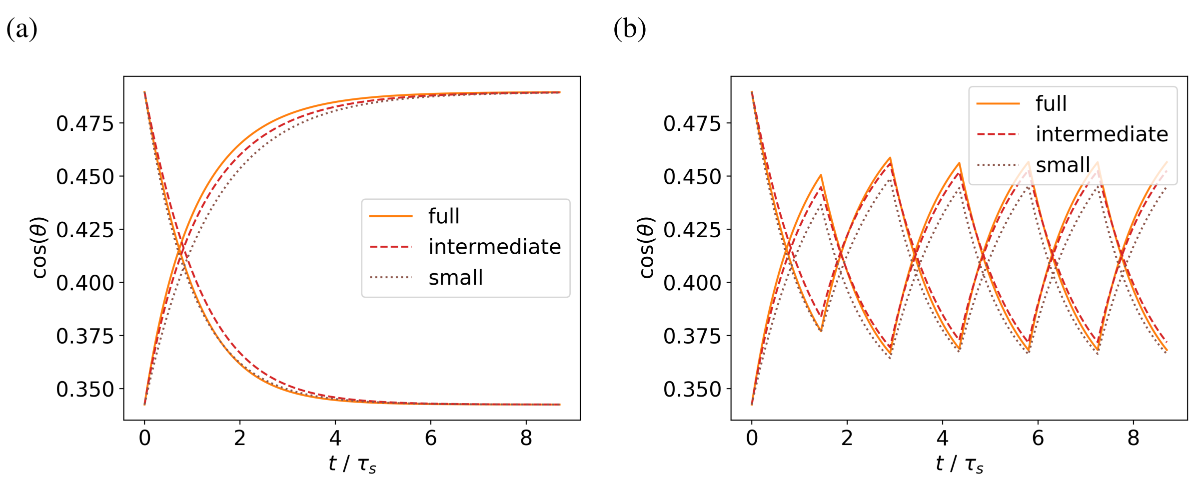

FIG. 4: Evolution of $\cos(\theta)$ for the different approximations of the MKT for (a) a single switch and (b) periodic switching between $\varepsilon_w = 0.632$ and $\varepsilon_w = 0.671$. (full: Eq. (10), intermediate: Eq. (11); small: Eq. (12))

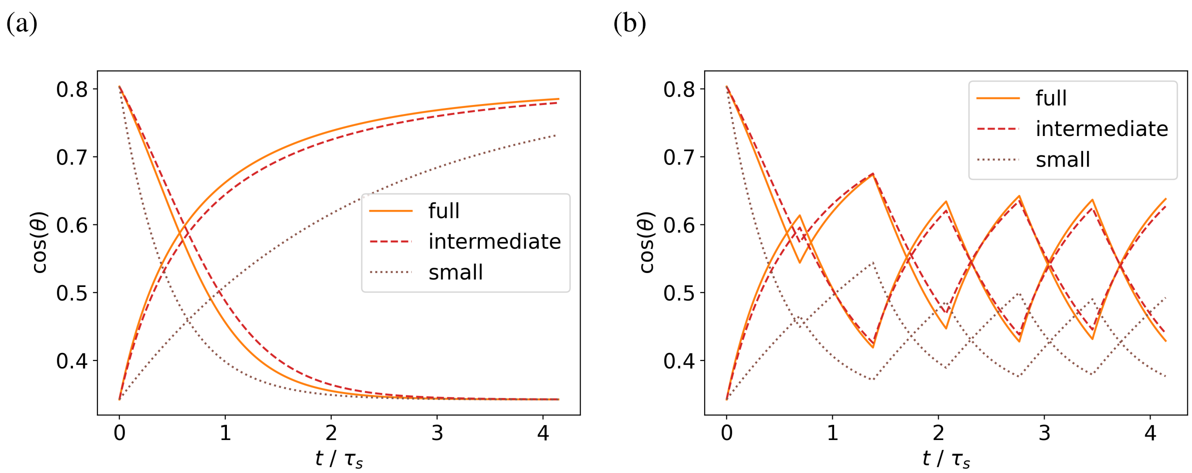

FIG. 5: Evolution of $\cos(\theta)$ for the different approximations of the MKT for (a) a single switch and (b) periodic switching between $\varepsilon_w = 0.632$ and $\varepsilon_w = 0.762$. (full: Eq. (10), intermediate: Eq. (11), small: Eq. (12))

From Eq. (11) after separation of variables one can write

$$\frac{dx}{(1-x)(x-x_{eq})} = -k_2 dt \tag{13}$$

Here and in the following, we will write x and x_{eq} for $\cos(\theta)$ and $\cos\left(\theta_{eq}\right)$, respectively, for reasons of better readability. Note that

$$\frac{1}{(1-x)(x-x_{eq})} = \frac{1}{1-x_{eq}}\left[\frac{1}{1-x} + \frac{1}{x-x_{eq}}\right] \tag{14}$$

Therefore, one obtains for the solution of the differential equation

$$-\ln(1-x) + \ln\left(x - x_{eq}\right) = -k_2(1-x_{eq})t + C \tag{15}$$

with the integration constant $C = -\ln(1-x_0) + \ln\left(x_0 - x_{eq}\right)$. Furthermore, we use the abbreviation $k_3 = k_2(1-x_{eq})$. Then we can rewrite

$$\frac{x - x_{eq}}{1-x} = \frac{x_0 - x_{eq}}{1-x_0}\exp(-k_3 t) \tag{16}$$

Finally, one needs to solve this equation for $x(t)$. After a short calculation one obtains

$$x(t) = \frac{x_{eq} + \varepsilon(t)}{1 + \varepsilon(t)} \tag{17}$$

with

$$\varepsilon(t) = \frac{x_0 - x_{eq}}{1 - x_0} \exp(-k_3 t) \tag{18}$$

For the normalized relaxation function $y(t) = (x(t) - x_{eq})/(x_0 - x_{eq})$ this yields

$$y(t) = \frac{(1 - x_{eq}) \exp(-k_3 t)}{1 - x_0 + \exp(-k_3 t)(x_0 - x_{eq})}. \tag{19}$$

For small but finite differences of $x_0 - x_{eq}$ (indicated by a small parameter $\Delta\varepsilon_w$) in order to learn more about the impact of increasing differences between the initial and the final state. For this purpose we take into account terms until ε^2. This yields

$$\begin{aligned} x(t) &= [x_{eq} + \varepsilon(t)[1 - \varepsilon(t) + \varepsilon(t)^2 + ...] \\ &\approx x_{eq} + (1 - x_{eq})(\varepsilon(t) - \varepsilon(t)^2) + ... \end{aligned} \tag{20}$$

Then we may write

$$y(t) \approx \frac{1 - x_{eq}}{1 - x_0} \left[\exp(-k_3 t) - \frac{x_0 - x_{eq}}{1 - x_0} \exp(-2k_3 t) \right]. \tag{21}$$

IV. ANALYTICAL CALCULATION OF WETTING PROPERTIES UPON PERIODICALLY SWITCHING

We start from the equation

$$\frac{d}{dt} y(t) = -k_{3,i}(y - a_i) \tag{22}$$

with a contact angle independent $k_{3,i}$ where i denotes the prefactor k_3 for an increasing ($\uparrow$) or decreasing ($\downarrow$) wettability. Its general solution reads

$$y(t) = a_i(1 - \exp(-k_{3,i} t)) + y(0) \exp(-k_{3,i} t) \tag{23}$$

As before, y is a normalized version of the cosine of the contact angle. Here, we first consider that before the first switching event the system is in the state of higher wettability. Then, in the first part of the switching experiment ($t \in [0, T/2)$) we have $a_\downarrow = 0$, in the second half $a_\uparrow = 1$ ($t \in [T/2, T)$). The period is denoted as T. Thus, for the first half switching period one obtains

$$y(t) = y(0) \exp\left(-k_{3,\downarrow} t\right) \tag{24}$$

and for the second half

$$y(t) = (1 - \exp\left(-k_{3,\uparrow} t\right)) + y(0) \exp\left(-k_{3,\downarrow} T/2\right) \exp\left(-k_{3,\uparrow} T/2\right) \tag{25}$$

The average over the first time interval is thus given by

$$\langle y_1 \rangle = y(0)\frac{1}{k_{3,\downarrow}T/2}\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right) \tag{26}$$

and that over the second time interval

$$\begin{aligned}\langle y_2 \rangle =& 1-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{k_{3,\uparrow}T/2}+y(0)\exp\left(-k_{3,\downarrow}T/2\right)\frac{1}{k_{3,\uparrow}T/2}(1-\exp\left(-k_{3,\uparrow}T/2\right))\\ =& 1-\frac{(1-\exp\left(-k_{3,\uparrow}T/2\right))}{k_{3,\uparrow}T/2}(1-y(0)\exp\left(-k_{3,\downarrow}T/2\right))\end{aligned} \tag{27}$$

The average over both time intervals finally reads

$$\begin{aligned}\langle y(0) \rangle =& \frac{1}{2}-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{2k_{3,\uparrow}T/2}+y(0)\left[\frac{1}{2k_{3,\downarrow}T/2}(1-\exp\left(-k_{3,\downarrow}T/2\right))\right.\\ &\left.+\exp\left(-k_{3,\downarrow}T/2\right)\frac{1}{2k_{3,\uparrow}T/2}(1-\exp\left(-k_{3,\uparrow}T/2\right))\right]\end{aligned} \tag{28}$$

Naturally, Eq. (28) also holds to express the average $\langle y(n) \rangle$ during the time $t = 2nT/2$ and $t = 2(n+1)T/2$ in dependence of $y(t = n \cdot T)$. Thus, we first need to find an explicit expression for $y(n)$. With the general solution given above, one can directly write (using the abbreviation $K_3 = k_{3,\downarrow} + k_{3,\uparrow}$)

$$y(t=T) = (1-\exp\left(-k_{3,\uparrow}T/2\right)) + y(0)\exp(-KT/2) \equiv C + Dy(0) \tag{29}$$

In general one has

$$y(t=n\cdot T)) = C + Dy(t=(n-1)\cdot T) \tag{30}$$

This recursive relation has a straightforward solution which reads (setting $y(0) = 1$)

$$\begin{aligned}y(t=n\cdot T) &= C(1+D+D^2+...+D^{n-1})+D^n = C\frac{1-D^n}{1-D}+D^n\\ &= \frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}(1-\exp(-K_3nT/2))+\exp(-K_3nT/2)\end{aligned} \tag{31}$$

Thus, we finally have

$$\begin{aligned}\langle y(n) \rangle =& \frac{1}{2}-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{2k_{3,\uparrow}T/2}\\ &+\left[\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}(1-\exp(-K_3nT/2))+\exp(-K_3nT/2)\right]\\ &\cdot\left[\frac{1}{2k_{3,\downarrow}T/2}(1-\exp\left(-k_{3,\downarrow}T/2\right))+\exp\left(-k_{3,\downarrow}T/2\right)\frac{1}{2k_{3,\uparrow}T/2}(1-\exp\left(-k_{3,\uparrow}T/2\right))\right]\end{aligned} \tag{32}$$

In the long-time limit one finds the plateau value

$$\begin{aligned}
\lim_{n\to\infty} y(t=n\cdot T) &= \frac{1}{2}\left\{1+\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}\frac{1}{k_{3,\downarrow}T/2}\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right)\right. \\
&\left.-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{k_{3,\uparrow}T/2}\left(1-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}\exp\left(-k_{3,\downarrow}T/2\right)\right)\right\} \\
&= \frac{1}{2}\left\{1+\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}\frac{1}{k_{3,\downarrow}T/2}\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right)\right. \\
&\left.-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{k_{3,\uparrow}T/2}\frac{1-\exp\left(-k_{3,\downarrow}T/2\right)}{1-\exp(-K_3T/2)}\right\} \\
&= \frac{1}{2}\left\{1+\frac{\left(1-\exp\left(-k_{3,\uparrow}T/2\right)\right)\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right.}{1-\exp(-K_3T/2)}\left(\frac{1}{k_{3,\downarrow}T/2}\right.\right. \\
&\left.\left.-\frac{1}{k_{3,\uparrow}T/2}\right)\right\} \equiv y_{plateau}
\end{aligned} \tag{33}$$

For very fast switching this boils down to

$$y_{plateau} = \frac{k_{3,\uparrow}}{K_3} - \frac{k_{3,\uparrow}-k_{3,\downarrow}}{24K_3}k_{3,\downarrow}k_{3,\uparrow}(T/2)^2 \tag{34}$$

The general equation for $y(n)$ can be rewritten with $y_{plateau}$

$$\begin{aligned}
\langle y(n)\rangle &= y_{plateau} + \exp(-K_3nT/2)\left(1-\frac{1-\exp\left(-k_{3,\uparrow}T/2\right)}{1-\exp(-K_3T/2)}\right) \\
&\cdot\left[\frac{1}{2k_{3,\downarrow}T/2}\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right)+\exp\left(-k_{3,\downarrow}T/2\right)\frac{1}{2k_{3,\uparrow}T/2}\left(1-\exp\left(-k_{3,\uparrow}T/2\right)\right)\right] \\
&\equiv y_{plateau} + \exp\left(-K(n+\frac{1}{2})T/2\right)\cdot\hat{y}_+
\end{aligned} \tag{35}$$

with

$$\begin{aligned}
\hat{y}_+ &= y\exp\left(\frac{K_3T}{4}\right)\frac{\exp\left(-k_{3,\uparrow}T/2\right)-\exp(-K_3T/2)}{1-\exp(-K_3T/2)} \\
&\cdot\left[\frac{1}{k_{3,\downarrow}T}\left(1-\exp\left(-k_{3,\downarrow}T/2\right)\right)+\exp\left(-k_{3,\downarrow}T/2\right)\frac{1}{k_{3,\uparrow}T}\left(1-\exp\left(-k_{3,\uparrow}T/2\right)\right)\right]
\end{aligned} \tag{36}$$

When starting from the state with lower wettability one ends up with

$$\langle y(n)\rangle = y_{plateau} - \exp\left(-K(n+\frac{1}{2})T/2\right)\cdot\hat{y}_- \tag{37}$$

$\hat{y}_-$ is identical to $\hat{y}_+$ after exchange of $k_{3,\downarrow}$ with $k_{3,\uparrow}$.

For $k_{3,\downarrow} = k_{3,\uparrow} = k_3$ these expressions simplify to

$$
\begin{aligned}
y(n) &= \frac{1}{2} + \exp\left(-k_3(2n+1)T/2\right)\frac{1-\exp(-k_3T/2)}{1-\exp(-2k_3T/2)}\frac{1}{2k_3T/2} \\
&+ (1-\exp(-k_3T/2))(1+\exp(-k_3T/2)) \\
&= \frac{1}{2} + \exp(-k_3(2n+1)T/2)\frac{1}{2k_3T/2}(1-\exp(-k_3T/2))
\end{aligned} \tag{38}
$$

V. ζ

Table Tab. I shows values of ζ_R extracted from the MD model with two different methods. ζ can be obtained via K_0, which is the inverse time needed for half the particles to move from the first to the second layer, and n, the density of the first liquid layer[1]. ζ_{MD} denotes the ζ value extracted from an analysis of the contact line velocity in dependence of the cosine of the contact angle.

TABLE I: Values of K_0, n, and ζ_R directly calculated from MD simulations as well as values of ζ_{MD} extracted from the analysis of the contact line velocity dependence on the cosine of the contact angle.

ε	K_0/τ^{-1}	n/σ^{-3}	ζ_R
0.447	$4.62\cdot10^{-4}$	0.57	$0.93\cdot10^{3}$
0.548	$3.81\cdot10^{-4}$	0.62	$1.23\cdot10^{3}$
0.632	$3.24\cdot10^{-4}$	0.66	$1.53\cdot10^{3}$
0.707	$2.76\cdot10^{-4}$	0.69	$1.88\cdot10^{3}$
0.742	$2.55\cdot10^{-4}$	0.70	$2.07\cdot10^{3}$
0.762	$2.44\cdot10^{-4}$	0.71	$2.19\cdot10^{3}$
0.809	$2.40\cdot10^{-4}$	0.71	$2.23\cdot10^{3}$
0.775	$2.17\cdot10^{-4}$	0.73	$2.51\cdot10^{3}$
0.837	$2.03\cdot10^{-4}$	0.74	$2.73\cdot10^{3}$

In the TF model the contact angle velocity can be analyzed analogously. The resulting values can be found in Tab. II.

TABLE II: Values of ζ_{TF} within the TF model extracted from the analysis of the contact line velocity dependence on the cosine of the contact angle

Initial ε	Final ε	ζ_{TF}
0.762	0.632	1.60
0.671	0.632	1.39
0.632	0.671	1.52
0.632	0.762	2.72

VI. STRETCHING/COMPRESSION OF THE RELAXATION

We have fitted a stretched exponential for the relaxation function after a single switching process which can be seen in Fig. 6 for TF and in Fig. 7 for MD data. The resulting β-values for the MD simulations, for the TF analysis, and for the MKT equations (Eq. 10) are listed in Tab. III.

TABLE III: Values of β obtained from an non-exponential fit to the data for a single switching event from ε_1 to ε_2 in MD, MKT and TF simulations.

ε_1	ε_2	β_{MD}	β_{MKT}	β_{TF}
0.632	0.762	0.87	0.73	0.68
0.762	0.632	1.68	1.42	2.05

One consistently observes a stretched exponential behavior when increasing the wettability upon switching and a compressed exponential behavior in the opposite case.

For the interpretation of possible non-exponential effects in relaxation functions $y(t)$ we start by defining the n-th moment of $y(t)$ as

$$\langle \tau^n \rangle = \frac{\int_0^\infty t^n \cdot y(t) \mathrm{d}t}{\int_0^\infty y(t)}. \tag{39}$$

Now, we can compute the quantity

$$\frac{\langle \tau^2 \rangle}{2\langle \tau \rangle^2}, \tag{40}$$

which is equal to one for a purely exponential function $y(t)$. If this quantity is greater than 1, it implies a compressed exponential function, i. e. $\beta > 1$ whereas in the opposite case it describes a stretched exponential function, i. e. $\beta < 1$.

For the $y(t)$, given in Eq. (21), we get

$$\frac{\langle \tau^2 \rangle}{2\langle \tau \rangle^2} = \frac{\left(1-\frac{B}{8}\right)\left(1-\frac{B}{2}\right)}{\left(1-\frac{B}{4}\right)^2} = 1 - \frac{B}{8(1-\frac{B}{4})^2}, \tag{41}$$

where $B = \frac{x_0 - x_{eq}}{1-x_0}$. For switching from higher to lower wettability $x_0 > x_{eq}$ holds, which implies $B > 0$. Consequently, the expression in Eq. (41) has to be smaller than 1 and finally β has to be greater 1. Analogously $\beta < 1$ follows for the inverse switching direction. This is in accordance with our results from the different models, as shown in Tab. III.

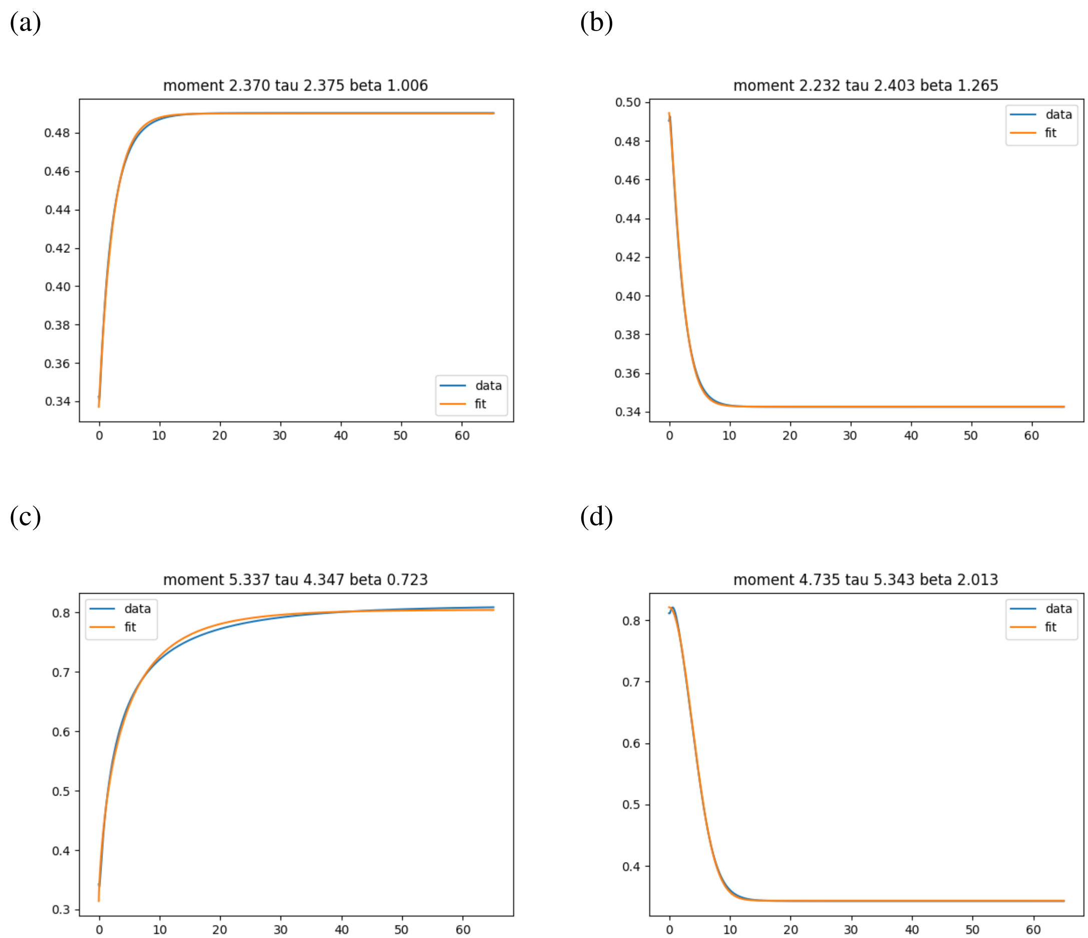

FIG. 6: Relaxation of $\cos(\theta)$ after an instantaneous change in wettability in the TF model for the wettability values corresponding to different changes in interaction strengths $\varepsilon_1 \rightarrow \varepsilon_2$ in the MD model: a) $0.632 \rightarrow 0.671$, b) $0.671 \rightarrow 0.632$, c) $0.632 \rightarrow 0.0.762$ and d) $0.762 \rightarrow 0.632$.

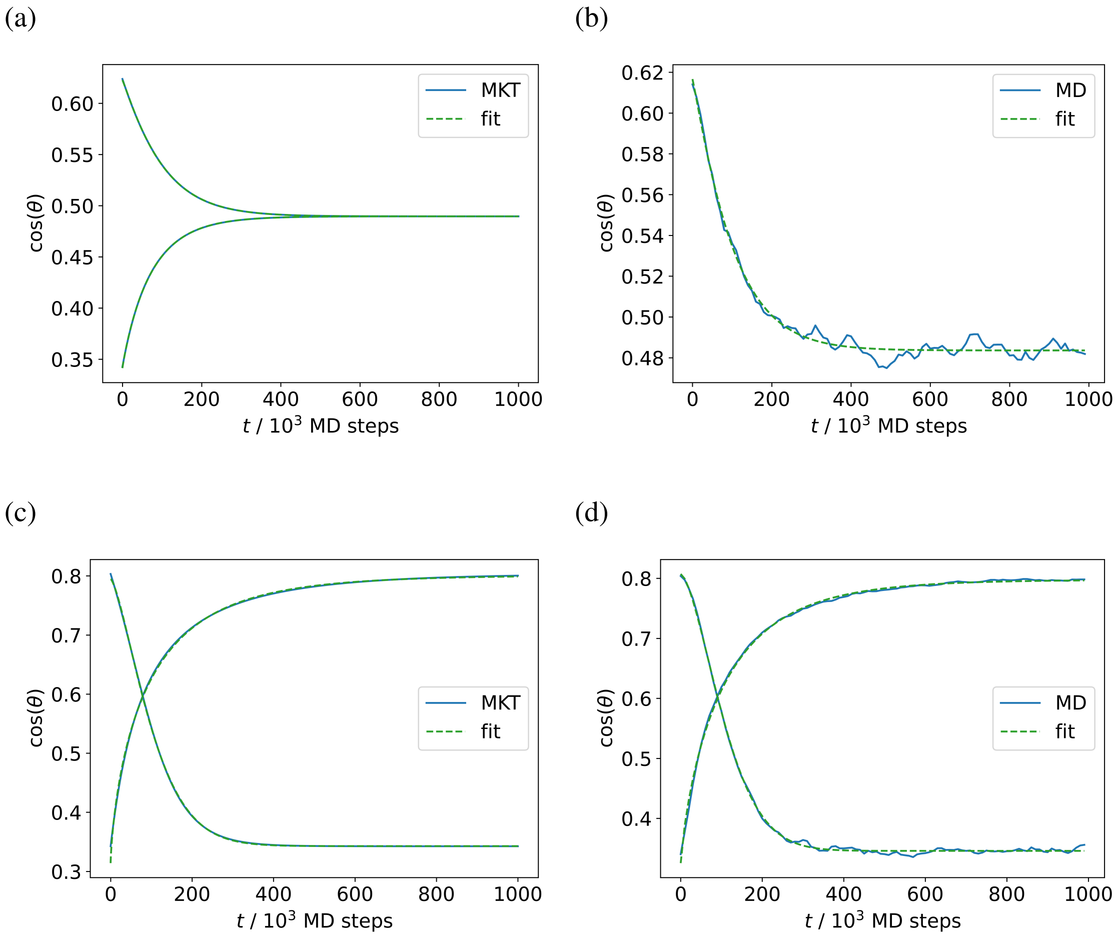

FIG. 7: Relaxation of $\cos\theta$ after an instantaneous change in wettability in the MD and MKT model for the interaction strengths $\varepsilon_1 \leftrightarrow \varepsilon_2$: (a) $0.632 \leftrightarrow 0.671$ (MKT), (b) $0.632 \leftrightarrow 0.671$ (MD), (c) $0.632 \leftrightarrow 0.762$ (MKT) and (d) $0.632 \leftrightarrow 0.762$ (MD).

VII. MINIMUM $y_{plateau}$ VALUE

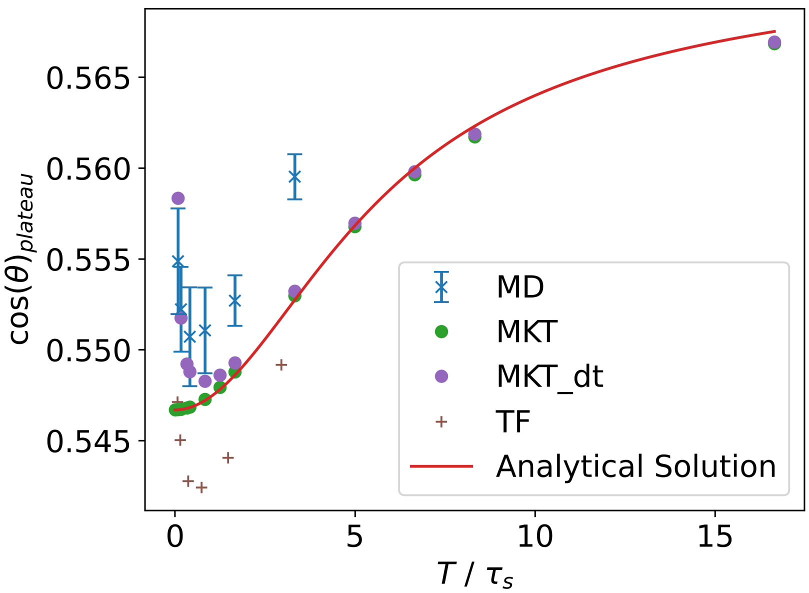

FIG. 8: (a) $\cos(\theta)_{\mathrm{plateau}}$ obtained from MD, MKT, MKT with a dead time effect (MKT_dt), TF and from the analytical solution given in Eq. (33) plotted against T for switching between $\varepsilon_{LW} = 0.632$ and $\varepsilon_{HW} = 0.762$.

For calculating the MKT values with short time effects in Fig. 8 we included a dead time where we set $\gamma/\zeta = 0$ after each switching event for 1500 time steps when switching to a higher wettability and $\frac{3}{4} \cdot 1500$ time steps when switching to a lower wettability. The factor of $\frac{3}{4}$ results from the relation of the time steps that show the nonlinear behavior in Fig. 9.

REFERENCES

[1]M. J. de Ruijter, T. D. Blake, and J. De Coninck, Langmuir **15**, 7836 (1999), https://doi.org/10.1021/la990171l.

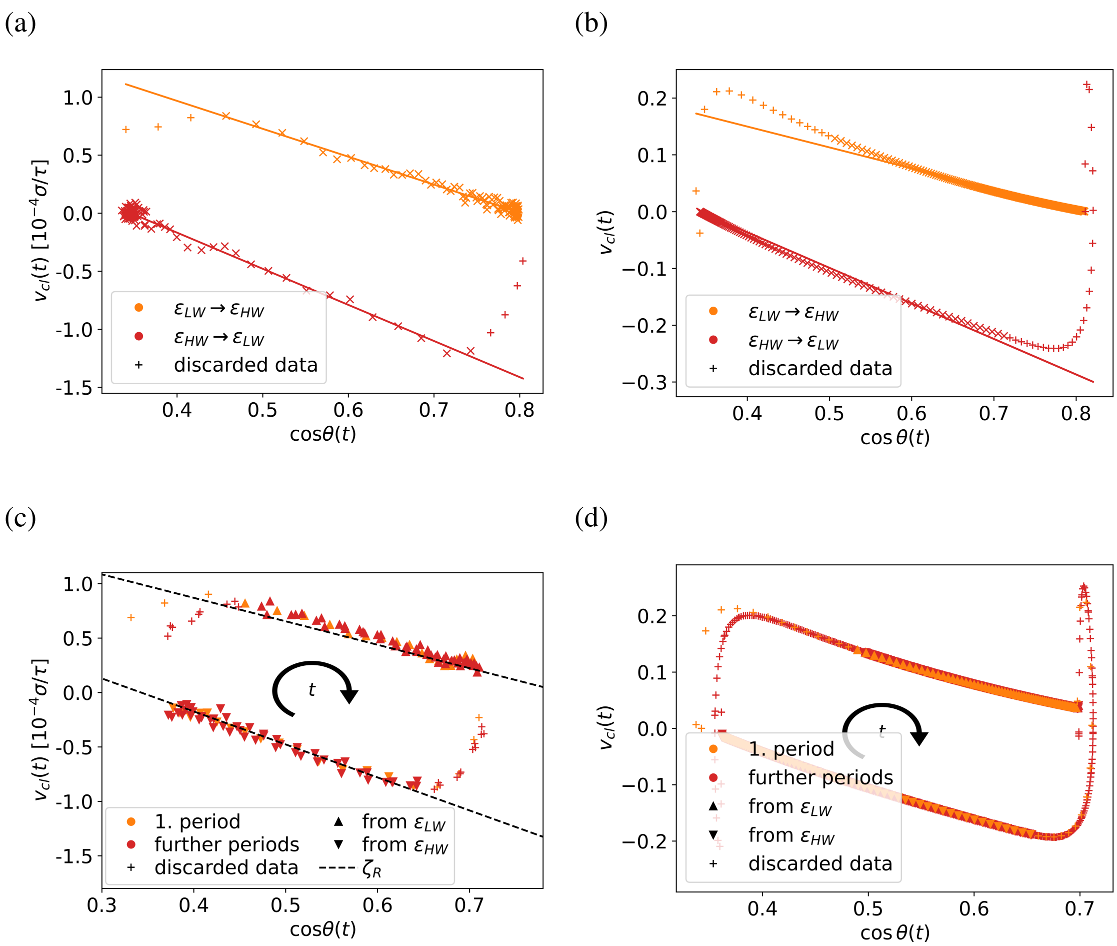

FIG. 9: Figure taken from main manuscript: Velocity of the contact line v_{cl} plotted against $\cos\theta(t)$ for (a) the relaxation of a droplet on a surface with a wettability change from $\varepsilon_{HW} = 0.762$ to $\varepsilon_{LW} = 0.632$ and the reverse process. A line is fitted to the data to compute ζ_{MD} from its slope according to the MKT theory. The first few data points (plus sign) were discarded for these fits. Data points are spaced equidistantly with $\Delta t = 10^4$ MD steps, (b) TF simulations corresponding to the MD results in (a) with $\Delta t = 0.1$. (c) v_{cl} plotted against $\cos\theta(t)$ for a droplet on a surface with a periodically switched wettability from $\varepsilon_{HW} = 0.762$ to $\varepsilon_{LW} = 0.632$ with the initial droplet equilibrated on a surface with a wettability of ε_{LW}. The switching period was $T = 2 \cdot 10^6$ MD steps. The data points are again spaced equidistantly with $\Delta t = 10^4$ MD steps. The dashed lines are plots of Eq. (9) with values of ζ_R for wettabilities of ε_{HW} and ε_{LW}, respectively. (d) The TF equivalent of (c) with $T = 15.8$ and $\Delta t = 0.1$. Note that there is no noise in the TF model.