Wetting behavior of droplets on switchable substrates: A theoretical perspective

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The development of substrates with a switchable wettability is on a fast pace. The limit of switching frequencies and contact angle differences between substrate states are steadily pushed further. We investigate the behavior of a droplet on a homogeneous substrate, which is switched between two wettabilities for a large range of switching frequencies. Here, we are particularly interested in the dependence of the wetting behavior on the switching frequency. We show, that results obtained on the particle level via molecular dynamics simulations and on the continuum level via the thin-film model are consistent. Predictions of a simple models as the molecular theory of wetting (MKT) and analytical calculations based on the MKT also show good agreement and offer analytical insights within the limits of the approximations employed.

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I. INTRODUCTION

Controlling and understanding the movement of droplets is mandatory for microfluidic, e.g. Lab-On-A-Chip devices. Surfaces with wettability gradients and adaptive substrates have been the focus of investigation for quite some time. Recent experiments have shown that coating a substrate with a self-assembled monolayer (SAM) of photoswitchable moieties like azobenzenes or spiropyranes leads to surfaces, whose wettability can be controlled by illumination with light of a defined wavelength which makes the control of the droplets motion possible by applying a light gradient. Another possible dynamical behaviour one can think of are oscillatory motions. This behaviour can be induced and were investigated in the context of e.g., vibrating plates or electrowetting. Oscillatory motions of droplets can show interesting effects like making a droplet move up on an inclined, vibrating plate. As such, the opportunity to change surface properties in time has a variety of applications, e.g. it can be used in devices, which measure liquid properties like surface tension. It can also be applied to mix liquids inside a drop, which again is useful for the design of Labs-On-A-Chip.

The emergence of a variety of novel surfaces with a switchable wettability property has led to increased efforts in the theoretical realm to advance the understanding of the dynamics of liquids on such surfaces.

Theoretical investigations of the dynamical behavior of droplets on surfaces with an oscillating wettability can be performed with a variety of different models depending on the time and spatial scales. For instance, the boundary element method applied to Stokes flow, mesoscopic models based on the lubrication approximation and microscopic models like molecular dynamics have all been successfully applied to dynamic wetting problems. The inherent complexity in such models often makes it hard to pinpoint the physical origin of effect in question and hence, comparison with minimal models can help to understand the physical effects at work.

In this work, we present numerical solutions of a mesoscopic Thin Film (TF) model and particle-based Molecular Dynamics (MD) simulations. In particular, we characterize the wetting behavior of droplets upon periodically varying wettabilities, resulting from the interaction of the droplet with the switchable surface. We compare our results to the molecular kinetic theory of wetting (MKT). After its introduction by Blake and Haynes, it was widely and successfully used in the context of dynamic wetting. The MKT expresses how the deviation of a non-equilibrium contact angle to its equilibrium value gives rise to a contact line velocity of the droplet, promoting
the approach to equilibrium. Note that in our mesoscopic and particle-based approaches the contact line velocity is inherent in the model. It is not, e.g., influenced by boundary conditions as in \textsuperscript{29} and does not need to be additionally imposed as in \textsuperscript{18}.

This paper is organized as follows: In Sec. II we explain our simulation setup of the MD and the TF theory and introduce the mapping procedure we used to compare both methods. Additionally, we introduce the background of the MKT and present some analytical solutions when applying the MKT to switchable substrates with periodic wettability changes.

For a quantitative comparison to the MKT, relevant input parameters need to be extracted from other models as presented in Sec. III A. Among others we refer to a method introduced by de Ruiter, Blake, and De Coninck\textsuperscript{26}. After checking the applicability of our mapping scheme in Section III B, we present the results obtained from the three methods (MD, TF, MKT) for the dynamics of a droplet on a periodically switched substrate and compare them in Section III C. Finally, we will conclude our results in Section IV.

II. THEORETICAL BACKGROUND

A. Molecular Dynamics Simulations

We use the same simulation setup as presented in \textsuperscript{30}. In particular, we are performing simulations in the NVT ensemble with the framework HOOMD\textsuperscript{31,32}. Two types of particles are present in the system, namely substrate particles (here denoted with the "s"), which are frozen in two layers of a fcc(111) surface and fluid particles (denoted with "f"). The particles interact through the Lennard-Jones potential

$$V(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right],$$

where $r_{ij}$ is the distance between two particles $i$ and $j$, $\varepsilon_{ij}$ the interaction strength between the particles and $\sigma_{ij}$ the arithmetic mean of the particles’ diameters $\sigma_i$ and $\sigma_j$. The potential is truncated and shifted at a cutoff-radius of $r_c = 2.5 \sigma$. The interaction strength $\varepsilon_{ij}$ of two particles is calculated as the geometric mean of the self-interaction parameters of both particles $\varepsilon_i$ and $\varepsilon_j$. We set $\varepsilon_f = 1$ and change the wettability of the substrate by varying the parameter $\varepsilon_s$ which then varies the interaction $\varepsilon_w$ between substrate and liquid particles which by construction is given as the geometric mean $\varepsilon_w = \sqrt{\varepsilon_s \cdot \varepsilon_f} = \sqrt{\varepsilon_s}$. The schematic in Fig. 1 visualises how switching works in this model with the example of periodic switching.
FIG. 1: Schematic of the periodic switching procedure. The droplet states, shown on the left and the right, respectively, correspond to the situation directly before switching to the other wettability (from violet to orange or vice versa). For very long switching periods $T$ they are the respective equilibrium states, otherwise they are non-equilibrium states. The top and bottom droplets express respective intermediate non-equilibrium states after the switching process. The central panel shows, how the parameters, responsible for the substrate’s wettability in MD and TF models, change with time (HW: high wettability; LW: low wettability).

We set the particles diameter to $\sigma_l = \sigma_s = \sigma$ for all particles and use a time step of $\tau = \sigma^{-1} \sqrt{\epsilon_f/M}/200$. The reduced temperature which is controlled by a dissipative particle dynamics (DPD) thermostat $^{33}$ is $k_BT/\epsilon_f = 0.75$, where $M$ is the particle mass. Periodic boundary conditions are present in the $x$- and $y$-direction. The substrate is placed in the $xy$-plane.

The domain size in $y$-direction is chosen in such a way that Plateau-Rayleigh instabilities are suppressed and the effect of line tension is excluded by simulating a cylindrical droplet. All simulations are carried out with a total amount of $N = 4 \cdot 10^4$ fluid particles. Every simulation setup is averaged over 50 trajectories.

To determine the contact angle of the droplet we calculate the density field of the fluid particles
by averaging over the $y$-direction. From this we can determine the position of the liquid vapor interface with a tanh-fit. Then we perform a circular fit to the positions of the liquid vapor interface for each liquid slab in $z$-direction and calculate the contact angle from this fit.

B. Thin film equation theory (TF)

On the mesoscopic scale, we model the evolution of the local height $h = h(x,y,t)$ of the film or a droplet with the well-established lubrication approximation that can be derived from the Navier-Stokes equation\cite{34}. For the simulation we employ the finite element library oomph-lib\cite{35}. We reduce the spatial dimension of the problem by assuming transversal symmetry in $y$-direction, i.e. we simulate cylindrical droplets and exclude transversal instabilities. It leads to an evolution equation in gradient dynamics form as\cite{36}

$$\partial_t h = \nabla \cdot \left[ M(h) \nabla \frac{\delta F}{\delta h} \right]$$

with the mobility $M(h)$ and the free energy functional $\mathcal{F} = \mathcal{F}[h]$. The no-slip boundary condition at the substrate leads to a mobility of $M(h) = h^3/(3\eta)$ with the dynamic viscosity $\eta$\cite{34}. The generalized pressure $P = \frac{\delta \mathcal{F}}{\delta h}$ is given by

$$P(h,x,t) = -\gamma \Delta h - \Pi(h,t)$$

with the surface tension $\gamma$ and the disjoining (or Derjaguin) pressure $\Pi(h,t)$. Different choices for the wetting potential and corresponding disjoining pressure are possible\cite{34}. Here, we choose

$$\Pi(h,t) = \left( \frac{C}{h^6} - \frac{D}{h^3} \right) (1 + \rho(t)).$$

with the interaction strengths of long and short ranging forces $C$ and $D$ respectively. $C$ can be directly connected to the Hamaker constant $H$ by $C = H/6\pi$\cite{37}.

Analogous to Honisch et al\cite{20} we incorporated a change in wettability by modulating the disjoining pressure\cite{36}. In Eq. (4) we call the parameter $\rho = \rho(t)$ wettability, because its value modulates the disjoining pressure and determines the current wettability of the system. To resolve the problem of a logarithmic energy dissipation at the contact line\cite{38}, which is a consequence of the no-slip boundary condition, a precursor film with height $h_p$ is introduced\cite{37,38}. Such a precursor film is also present on macroscopically “dry” parts of the substrate.
The oomph-lib numerical implementation is based on the non-dimensionalized form of Eq. (2), where the quantities $h$, $x$ and $t$ are scaled in such a way, that $\gamma$, $C$, $D$ and $3\eta$ vanish from the evolution equation, yielding

$$\partial_t h = \nabla \cdot \left\{ h^3 \nabla \left( -\Delta h - \frac{5}{3} \theta_{eq}^2 \chi^2 \left( \frac{\chi^3}{h^6} - \frac{1}{h^3} \right) [1 + \rho(t)] \right) \right\}$$

with the equilibrium contact angle $\theta_{eq}$ and the parameter $\chi = h_p/h_0$, where $h_0$ is the spatial scale. In what follows, for further analysis we subtract the precursor film height $h_p$ from the film height $h$ in Eq. (5). In all the simulations presented here, we use $\chi = 0.01$.

C. Mapping between TF and MD

The substrate wettability in the MD model is introduced via the interaction strength between solid and liquid $\varepsilon_w$, whereas in the TF model the disjoining pressure is modulated via the parameter $\rho$ to account for different substrate wettabilities. For a static mapping between both parameters the resulting contact angle of a equilibrated droplet at a certain wettability parameter can be used. However, in the TF model the contact region exhibits a smooth transition to the precursor film and there is no sharp contact line. Also the underlying lubrication approximation makes droplets in the TF model deviate from a strict spherical cap shape. Thus, contact angle measurements in the TF model are finicky. Even the method for the measurement can make a difference\(^{39}\). Instead of direct contact angle measurements we use the relative full width at half maximum $r_{FWHM}$, which is the width at half maximum in relation to the drop height. This measure can be determined stably and does not depend on the contact region. Also, the contact angle can be directly computed for a given $r_{FWHM}$ according to

$$\cos(\theta) = 1 - \frac{4}{r_{FWHM}^2 + 1},$$

which can be derived based on the assumption of a spherical cap shape. The derivation can be found in SI.\(^{[A]}\) With the help of parameter scans in both wettability parameters we obtained an invertible mapping $\varepsilon_w \mapsto \rho$ based on $r_{FWHM}$. To avoid confusion between these parameters we only mention the relevant $\varepsilon_w$ values and mean the corresponding $\rho$ value, when showing TF results.

To match the time scales we can use a characteristic time like a relaxation time. As the relaxation of $\cos \theta$ does not necessarily has an exponential shape, we fit the evolution of the measure
\[ \cos \theta(t) \] with a stretched exponential function

\[ f(t) = f_\infty + (f_0 - f_\infty)e^{-\left(\frac{t}{\tau}\right)^\beta}. \]  

(7)

We define the first moment as

\[ \tau_s = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \]  

(8)

where \( \Gamma \) is the gamma function. We use the definition of Eq. (8) to define the relaxation time of \( f(t) \). In section III.B we show how this procedure is applied.

D. Molecular Theory of Wetting

The molecular kinetic theory of wetting (MKT)\(^{25}\) accounts for the dissipation of a moving droplet in the contact line region. This yields an equation which relates the velocity of the three phase contact line \( v_{cl} \) to the time dependent cosine of the contact angle \( \cos(\theta(t)) \)

\[ v_{cl} = \frac{\gamma}{\zeta}(\cos(\theta_{eq}) - \cos(\theta(t))). \]  

(9)

Here, \( \gamma \) is the surface tension, \( \zeta \) a friction coefficient and \( \theta_{eq} \) the equilibrium contact angle. In general, the ratio \( \gamma/\zeta \) can be obtained from measuring the contact line velocity in dependence of the contact angle. On a deeper level, as shown below, for the particle-based model the values of \( \gamma \) and \( \zeta \) can be separately estimated from additional MD simulations.

If we assume a circular shape of the droplet during the whole spreading or contracting process we can rewrite Eq. (9) as

\[ \frac{d}{dt} \cos(\theta) = k_1 \frac{\sin(\theta)}{g(\theta)} (\cos(\theta_{eq}) - \cos(\theta)) \]  

(10)

with

\[ g(\theta) = \frac{\cos(\theta)}{(2\theta - \sin(2\theta))^{\frac{1}{2}}} - \frac{\sin(\theta)(1 - \cos(2\theta))}{(2\theta - \sin(2\theta))^{\frac{3}{2}}} \]  

(11)

and \( k_1 = \frac{\gamma/\zeta}{\sqrt{2A}} \) where \( A \) is the volume of the 2D droplet (cf. SI.B). In good approximation \( \frac{\sin(\theta)}{g(\theta)} \) can be written as \( 3(1 - \cos(\theta)) \) in the whole range of contact angles relevant for a comparison to the TF model (cf. SI.B for details). As a consequence, Eq. (10) can be simplified as

\[ \frac{d}{dt} \cos(\theta) = k_2 (1 - \cos(\theta))(\cos(\theta_{eq}) - \cos(\theta)), \]  

(12)

where \( k_2 = 3k_1 \).
Now we present analytical solutions, based on Eq. (12), for which the details are provided in the Supplementary Information. First we study the case of the time evolution of a droplet after a single switching process. In what follows we denote \( \cos(\theta(t)) \) as \( x(t) \). Its value before the switching process is denoted \( x_0 \). Here we assume that this is the equilibrium value, corresponding to the initial wettability. Furthermore, its equilibrium value, reached in the long-time limit after the switching process, is denoted \( x_{eq} \). Finally, we introduce

\[
y(t) = \frac{x(t) - x_{eq}}{x_0 - x_{eq}} \tag{13}
\]

which is the normalized version of \( x(t) \), with the properties \( y(t = 0) = 1 \) and \( y(t = \infty) = 0 \). After a short calculation (cf. SI. B) one obtains

\[
y(t) = \frac{(1 - x_{eq}) \exp(-k_3 t)}{1 - x_0 + \exp(-k_3 t)(x_0 - x_{eq})}, \tag{14}
\]

with \( k_3 = k_2(1 - x_{eq}) \). When identifying the average relaxation time \( \langle \tau \rangle \) with the integral over the normalized relaxation function \( y(t) \) one gets after a straightforward calculation

\[
\langle \tau \rangle = \frac{1}{k_2} \frac{\ln \left( 1 + \frac{x_0 - x_{eq}}{1 - x_0} \right)}{x_0 - x_{eq}} \tag{15}
\]

For \( |x_0 - x_{eq}| \ll 1 \), i.e. small wettability changes, one can also use the approximated (cf. SI. B) form

\[
y(t) \approx \frac{1 - x_{eq}}{1 - x_0} \left[ \exp(-k_3 t) - \frac{x_0 - x_{eq}}{1 - x_0} \exp(-2k_3 t) \right]. \tag{16}
\]

The second analytical solution directly starts from the limit of small wettability changes. In this limit \( x(t) \) is always close to \( x_{eq} \) so that in Eq. (12) we may approximate the prefactor \( 1 - x(t) \) as \( 1 - x_{eq} \), yielding

\[
\frac{d}{dt} x(t) = k_3 (x_{eq} - x(t)), \tag{17}
\]

with \( k_3 = k_2(1 - x_{eq}) \). Indeed, this is the same definition of \( k_3 \) as automatically resulting in the exact calculation in Eq. (14). For the sake of simplicity we again use the normalized version of the cosine of the contact angle \( y(t) \) so that we can write Eq. (17) as

\[
\frac{d}{dt} y(t) = -k_{3,i} (y - a_i), \tag{18}
\]

where \( k_{3,i} \) and \( a_i \in \{0, 1\} \) are the prefactor and the normalized equilibrium contact angle, respectively. Now we take into account that the wettability is periodically varied, one full cycle taking a time \( T \). Starting from a droplet equilibrated at a higher wettability (corresponding to the normalized contact angle \( a = 1 \)) we set \( i = \downarrow \) and \( a_1 = 0 \) for the first half of a switching period and \( i = \uparrow \)
and \( a_2 = 1 \) for the second half of the period (cf. the schematic in Fig. 1). After some calculations (cf. SI. C for details) the normalized cosine of the contact angle averaged over one period can be derived as

\[
\langle y(n) \rangle = y_{\text{plateau}} \pm e^{-K(n + \frac{1}{2})T/2} \cdot \hat{y}
\]  

(19)

with \( K = k_{3,\downarrow} + k_{3,\uparrow} \). \( \langle y(n) \rangle \) denotes the average of \( y(t) \) between \( t = nT \) and \( t = (n + 1)T \) and is evaluated at the time \( t = (n + 1/2)T \). The \( \pm \) distinguishes an initial higher wettability (\( + \)) from an initial lower wettability (\( - \)). The plateau value \( y_{\text{plateau}} \), obtained in the limit of an infinite number of switching cycles \( n \), is given by

\[
y_{\text{plateau}} = \frac{1}{2} \left\{ \frac{1}{2} \left( \frac{1 - \exp(-k_{3,\downarrow}T/2)}{1 - \exp(-K_3T/2)} \right) \right. \\
\left[ \frac{1}{k_{3,\downarrow}T/2} - \frac{1}{k_{3,\uparrow}T/2} \right] + 1 \}
\]  

(20)

This expression is independent of the starting wettability. In the limit case for very fast switching \( T \to 0 \) Eq. (20) boils down to

\[
y_{\text{plateau}} = \frac{k_{3,\downarrow}}{k_{3,\downarrow} + k_{3,\uparrow}} - \frac{k_{3,\uparrow} - k_{3,\downarrow}}{96(k_{3,\downarrow} + k_{3,\uparrow})} k_{3,\downarrow} k_{3,\uparrow} T^2.
\]  

(21)

For the amplitude we have to take care of the initial condition. If we start with the higher wettability, the amplitude \( \hat{y} \) from Eq. (19) turns out to be

\[
\hat{y} = e^{-k_{3,\downarrow}T/2} \frac{\exp(-k_{3,\downarrow}T/2) - \exp(-K_3T/2)}{1 - \exp(-K_3T/2)} + \left[ \frac{1}{2k_{3,\downarrow}T/2} \right] \\
+ (1 - e^{-k_{3,\downarrow}T/2}) + e^{-k_{3,\downarrow}T/2} \frac{1}{2k_{3,\uparrow}T/2} \left( 1 - e^{-k_{3,\uparrow}T/2} \right)
\]  

(22)

The expression for the other limit can be obtained by exchanging \( k_{3,\downarrow} \) with \( k_{3,\uparrow} \). We remind again that this analytical result only holds for small changes of the contact angle.

Although this calculation has been performed for small changes of the wettability, the range of applicability can be increased. Guided by Eq. (10) one may substitute \( k_1 \sin(\theta)/g(\theta) \) by \( k_1 \sin(\langle \theta \rangle)/g(\langle \theta \rangle) \). \( k_{3,j} \) in Eq. (19) and all corresponding formulas can be substituted by this value. Convenient is the choice \( \cos \theta = (1/2)(\cos \theta_{eq}(\varepsilon_{HW}) + \cos \theta_{eq}(\varepsilon_{LW})) \) which is the average angle for large switching times \( T \). Indeed, this is as shown below, the value of \( \langle y \rangle \) in the limit of an infinitely long period. The resulting value, is then denoted \( k_{3,j} \) which would substitute the corresponding value of \( k_{3,j} \).
III. RESULTS

A. MKT

The friction coefficient \( \zeta \) can be directly computed from quantities calculated from MD simulations as shown by de Ruijter, Blake, and De Coninck\(^{40}\) (further on denoted as ‘\( \zeta_{MD} \)’). It can be expressed as

\[
\zeta = \frac{n k_b T}{K_0 \lambda},
\]  

(23)

where \( n \) is the number of absorption sites per unit area on a solid, \( K_0 \) is the equilibrium frequency for particle displacements parallel to the solid and \( \lambda \) is the characteristic length of the displacement. We adopt the scheme of that reference to determine \( K_0 \) as the inverse of the time where half of the particles have moved between the first and second liquid layer in \( z \)-direction. We set \( \lambda = 1 \sigma \) since this is the distance between the first two liquid layers over the substrate and \( n \) is taken to be the density of the first liquid layer. The measured values of \( K_0, n \) and the resulting value of \( \zeta_{MD} \) via Eq. (23) can be found in SI D.

The obtained value of \( \gamma = (0.477 \pm 0.005) \epsilon / \sigma^2 \) is comparable to values from the literature for similar systems\(^{41}\). It was calculated by simulating a slab of liquid, which was placed in the \( xy \)-plane between its own vapor phase, and integrating the difference between the normal \( p_n \) and tangential \( p_t \) part of the pressure tensor over the box length in \( z \)-direction\(^{42}\)

\[
\gamma = \int dz \left( p_n(z) - p_t(z) \right).
\]  

(24)

Finally, the resulting ratios \( \zeta / \gamma \) are shown in Fig. 2 in dependence of the squared wetting energy \( \epsilon_w^2 \) which to a good approximation displays a linear behavior.

Another option to determine \( \zeta \) is to calculate the slope of a linear fit of \( v_{cl} \) versus \( \cos \theta(t) \) (denoted with ‘\( \zeta_{fit} \)’). This slope corresponds to the prefactor \( \zeta \) of equation (9) so that \( \zeta_{fit} \) can be determined by dividing the interface tension by the slope of the fit. Therefore, we equilibrated a droplet on a substrate with a lower solid-liquid interaction of \( \epsilon_{LW} \) and switched it instantaneously to a higher solid-liquid interaction \( \epsilon_{HW} \) or vice versa and calculated the contact angle during the relaxation process of the droplet. As can be seen in Fig. 3a) the first few data points do not show a linear behavior of the contact line velocity as obtained for later time steps. This effect is a result of calculating the contact angle from a circle fit. The droplet starts adapting to changes in the substrate’s wettability in the contact region and this influences the contact angle obtained from the
FIG. 2: (a) Values of $\zeta_{MD}$ and $\zeta_{fit}$ plotted against $\varepsilon_w^2$. The solid line is a linear fit through the values of $\zeta_{MD}$. ▲ and ▼ marks values of $\zeta_{fit}$ calculated from simulations where the wettability of the surface is changed by $\Delta \varepsilon_w = 0.05$ from a higher wettability ▼ and from a lower wettability ▲, respectively. ● marks values obtained from fits of Eq. (9) for switching between $\varepsilon_w = 0.632$ and $\varepsilon_w = 0.762$. The error bars show one standard deviation errors. (b) $\zeta_{fit}$ plotted against $\varepsilon_w^2$ for TF simulations.

As soon as the whole droplet is adapting to the change in wettability the relation between $v_{cl}$ and $\cos \theta$ is linear. However, a contact angle, based on the overall shape of the droplet is an important observable, since in experiments the contact angle is often measured in this way. As a consequence the first few data points for both switching directions cannot be used for the linear fit to determine $\zeta_{fit}$ indicated by the solid line in the figure. Like this $\zeta_{fit}$ can be determined for multiple pairs of $\varepsilon_{LW}$ and $\varepsilon_{HW}$ (cf. SI F). The resulting values are shown in Fig. 2 a) where $\zeta_{MD}/\gamma$ and $\zeta_{fit}/\gamma$ are plotted against $\varepsilon_w^2$. It shows that $\zeta$ increases with an increasing wettability since the particles are attracted more by the surface and thus the friction increases. Also it emphasizes the applicability of the scheme to calculate $\zeta_{MD}$ since the values of $\zeta_{MD}$ and $\zeta_{fit}$ agree very well. Furthermore, we would like to stress that within the statistical uncertainties $\zeta_{fit}$ does not depend on the switching direction and just reflects the interaction of the droplet with the substrate close to the contact line. This is in accordance with the physical picture of the MKT approach.

As shown in Fig. 3 b) the same phenomena are observed when analysing the velocity of the contact line for the TF data. This holds in particular for the artificial initial velocities, reflecting...
the strong deviations from a circular behavior close to the contact line. Furthermore, due to the absence of noise effects one can see very clearly the linear dependence of that velocity on the cosine of the contact angle, once this initial time regime is left. In analogy to the MD data we find again a mostly linear relation between $\zeta_{fit}$ and $\varepsilon^2_w$. Only for high values of the squared wettability energy $\varepsilon^2_w$ the values of $\zeta_{fit}/\gamma$ start to deviate from the linear behavior and also start to depend on the switching direction.

To check whether the MKT is also applicable to the case of periodic switching (emerging questions are if the non-linear periods of $v_{cl}$ versus $\cos(\theta)$ at the beginning of each switching event are on the same time scale for each switching period or if the shape of the droplet at the beginning of each switching events has impact on the results of the MKT) we simulate periodic switching by first equilibrating a droplet on a substrate with a constant interaction strength of $\varepsilon_{LW}$ or $\varepsilon_{HW}$, respectively. Then, at time $t = 0$ we start to periodically change the wettability of the substrate between $\varepsilon_{LW}$ and $\varepsilon_{HW}$ each $T/2$ time steps.

Figure 3 c) shows the result for such a periodically switched substrate. Linear fits of the data points after each change in wettability show comparable slopes to the single switch scenario in Fig. 3 a). This holds for later switching cycles as well. Also the dashed lines, which show Eq. (9) with values of $\zeta_{MD}$ for the corresponding wettabilities, confirm again that the values of $\zeta_{MD}$ and $\zeta_{fit}$ agree well. The same phenomena are seen for the TF data in Figure 3 d).

Naturally, knowledge about the velocity of the contact line should contain the relevant information to predict the relaxation behavior of $\cos(\theta(t))$. This is first explicitly explored for a single switching event. For this purpose we determine $\cos(\theta(t))$ after a single switching event and fit the resulting curve by a stretched exponential. The resulting relaxation times, using Eq. (8), are listed in Tab. I both for the TF and the MD data. As a comparison we use the input from the MKT analysis, namely the values of $\zeta_{fit}/\gamma$ to predict the expected switching times according to Eq. (15). They are also listed in Tab. I as $\tau_\zeta$. Indeed, one can find a reasonable agreement between both approaches. Part of the deviations may result from the introduction of the $1 - \cos(\theta)$-factor to enable the analytical calculation. Naturally, the time slightly depends on the switching direction.

B. Mapping between TF and MD

To establish a time mapping between TF and MD for a given pair of wetting energies ($\varepsilon_{LW}$, $\varepsilon_{HW}$) we take the value of $\tau_s$ when switching from $\varepsilon_{LW}$ to $\varepsilon_{HW}$. The resulting switching curves
FIG. 3: 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 $\zeta_{fit}$ from its slope according to the MKT theory. The first few data points (plus sign) were discarded for these fits. (b) TF simulations corresponding to the MD results in (a). (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 $\varepsilon_{LW}$. The switching period was $T = 40 \cdot 10^4$. The dashed lines are plots of Eq. (9) with values of $\zeta_{MD}$ for wettabilities of $\varepsilon_{HW}$ and $\varepsilon_{LW}$, respectively. (d) The TF equivalent of (c). Note, that there is no noise in the TF model.

for our standard example $\varepsilon_{LW} = 0.632$ and $\varepsilon_{HW} = 0.762$, using the dimensionless time axis, are shown in Fig. 4. Indeed, one can see that in this representation the MD and the TF data agree very well. By construction the function for the transition to the high wettability state decays on the time
TABLE I: Moments $\tau_s$ obtained from a fit of a stretched exponential to the values of $\cos(\theta)$ versus $t$ for switching from $\epsilon_1$ to $\epsilon_2$ for MD, MKT and TF simulations.

| $\epsilon_1$ | $\epsilon_2$ | $\tau_s$ (MD) | $\tau_s$ (TF) | $\tau_\zeta$ (MD) | $\tau_\zeta$ (TF) |
|--------------|--------------|----------------|----------------|-------------------|-------------------|
| 0.632        | 0.671        | $7.29 \cdot 10^4$ | 2.370         | $11.26 \cdot 10^4$ | 2.02              |
| 0.671        | 0.632        | $8.14 \cdot 10^4$ | 2.232         | $8.43 \cdot 10^4$  | 1.79              |
| 0.632        | 0.762        | $12.78 \cdot 10^4$ | 5.337         | $17.06 \cdot 10^4$ | 4.33              |
| 0.762        | 0.632        | $11.90 \cdot 10^4$ | 4.735         | $10.32 \cdot 10^4$ | 2.63              |

FIG. 4: $\cos(\theta)$ obtained from MD and TF simulation plotted against $t$ for a single switch. The corresponding values of $\epsilon_w$ are 0.632 and 0.762.

Note that in Fig. 4 not only the time scales but also the degree of non-exponentially is comparable between the MD and TF approach. Indeed, as discussed in SI.E and qualitatively seen...
in Fig. 4 when switching to the state of lower wettability one observes a stretched exponential whereas in the opposite case a compressed exponential is observed. This can be fully rationalized by the properties of the analytical solution in Eq. (16) (see SI.E).

C. Periodic Switching

A periodic switching procedure as described above yields an oscillating state around a plateau value of \( \cos(\theta) \) \(_{\text{plateau}}\) after an initial relaxation. This is shown for MD simulations in Fig. 5(a) and the TF simulations in Fig. 5(b) where the wettability of the surface is switched with a period of \( T = 1.524 \tau_s \). For the MD simulation we have added the numerical integration of the MKT equations Eq. (10). The MKT resembles the MD values for switching remarkably well despite an offset. This offset of the MKT in Fig. 5(a) mirrors that initially \( v_{cl} \) does not depend linearly on \( \cos \theta \) since the short time behavior of the contact angle from a circle fit is not included in the MKT. However, if the MKT values were shifted by \( \sim 0.2 \tau_s \) which is approximately the time of the nonlinear behavior at the beginning of each switching event MD and MKT would agree almost perfectly. This shows that MKT can reproduce MD results also for switching by a lot less computational effort, if you take into account, that short time effects cannot be reproduced which, to a good approximation may be regarded as a dead time.

Most importantly, from these data we determine the average values of \( \cos(\theta) \) during the individual switching periods \( \cos(\theta)_{MA} \) as shown in Fig. 5(a) and (b). These simulations have been repeated for different switching periods as well as for two different pairs of wetting energies, reflecting the case of small changes of the contact angle in Fig. 5(c) and (d) as well as the case of large changes of the contact angle in (e) and (f).

It is noticeable, that the plateau value of \( \cos(\theta)_{MA} \) is approximately the average \( \cos(\theta) \) of the corresponding equilibrium states but seems to be very slightly dependent on the switching period. This clearly can be seen in the \( \cos(\theta)_{MA} \) versus \( t \) plot for TF simulations since no noise is present. Also the analytical solution for Eq. (17) given in Eq. (19) is plotted in Fig. 5(c). It agrees remarkably well with the MD results obtained for switching between wettability energies of \( \epsilon_{LW} = 0.632 \) and \( \epsilon_{HW} = 0.671 \). Naturally, for the other case the difference of the contact angle is too large to justify the approximations made in the derivation of Eq. (19). Therefore, a comparison to the data in Fig. 5(e) is not possible.

Now we interpret the different properties, seen in Figs. 5(c)-(f). First, we display the average
FIG. 5: (a) The solid line shows the cosine of the contact angle $\cos(\theta)$ plotted against $t$ for a switching period of $T = 1.524\tau_s$. The triangles mark the average cosine of the contact angle over one period $\cos(\theta)_{MA}$ and the dashed line shows the results obtained from the MKT. (b) Corresponding results in the TF model for a switching period of $T = 1.478\tau_s$. (c) $\cos(\theta)_{MA}$ for different periods from 1 to 40 $T_{0,MD}$, where $T_{0,MD} = 7.62 \cdot 10^{-2}\tau_s$ while periodically switching the surface between $\varepsilon_{LW}$ and $\varepsilon_{HW}$. (d) TF simulations with corresponding wettability parameters, where $T_{0,TF} = 7.39 \cdot 10^{-2}\tau_s$. 


FIG. 6: (a) $\cos(\theta)$\(_{plateau}\) obtained from MD, MKT, TF and from Eq. (20) plotted against $T$ for switching between (a) $\varepsilon_{LW} = 0.632$ and $\varepsilon_{HW} = 0.762$ and (b) $\varepsilon_{LW} = 0.632$ and $\varepsilon_{HW} = 0.671$.

of $\cos(\theta)$ over one period $\cos(\theta)_{MA}$ versus the time for different switching periods. To better grasp the differences of the plateau values we averaged the values of $\cos(\theta)_{MA}$ up from a time step of $50 \cdot 10^4$ MD steps and plotted $\cos(\theta)_{plateau}$ against $T$ in Fig. 6. There, small changes in $\cos(\theta)_{plateau}$ in dependence of $T$ can be seen for MD and MKT as well as for TF simulations (note the scaling of the y-axis, $\cos(\theta)$ for droplets equilibrated at the corresponding high and low wettabilities are (a) $\sim 0.34$ and $\sim 0.80$ and (b) $\sim 0.34$ and $\sim 0.49$). Additionally, it is noticeable that $\cos(\theta)_{plateau}$ does not increase monotonically but reaches a local minimum for small values of $T$. This behavior can be seen for MD as well as for values obtained from TF simulations. Especially simulations with a higher $\Delta\varepsilon_w$ show this effect since it is not that much overlaid by noise. It can be attributed to short time dynamics of the contact angle obtained from the circle fit. By comparing the MD results with the ones obtained from the MKT theory with Eq. (20) where we resubstituted $k_{3,i}$ with $\tilde{k}_{3,i}$ this minimum is not observable since the unmodified MKT equation does not include these short time dynamic effects. By including these effects and changing the $\zeta$ value for the first few time steps it is in general possible to observe a minimum also in calculations based on the MKT theory. A qualitative example can be found in SI. The fact that values of $\cos(\theta)_{plateau}$ obtained from MD simulations are in general a bit higher can also possibly explained with these dynamics.

By analyzing Eq. (19) it is noticeable that the time scale of relaxation is neither dependent on the switching period nor on whether the switching process is started from a droplet equilibrated
FIG. 7: (a) and (b) moments resulting from stretched exponential fits to $\cos(\theta)_{MA}$ versus $t$ from MD and TF data respectively for switching between $\varepsilon = 0.632$ and $\varepsilon = 0.762$. (c) and (d) moments resulting from stretched exponential fits to MD and TF data respectively for switching between $\varepsilon = 0.632$ and $\varepsilon = 0.671$. The circles in (b) and (d) indicate the moments for the limit $T \to 0$, i.e. an effective wettability.

on a substrate with the higher or lower wettability. To obtain that time scale from the MD and TF simulations and the MKT results obtained with Eq. (10) we again fitted stretched exponentials to the data and calculated the respective time scale with Eq. (8). Here, a slight dependence on the starting configuration can be seen which may reflect the deviations from the ideal MKT equations as already discussed above. However, importantly the time scale hardly varies with the switching period as can be seen in Fig. 7 in full agreement with the MKT picture.

Finally, we study the dependence of the amplitude on the switching frequency. For the am-
plitude the analytical solution given in Eq. (22) overlaps very well with the results from the MD and MKT simulations even for higher changes in wettability. In Fig. 8 it can be seen that the amplitude decreases with $T$. In (d) one would expect the circles agree well with the analytical solution. The lower circle belongs to a simulation, where the effective wettability is higher than the initial wettability. In such a case $\cos(\theta)$ exhibits a small dip before it starts to increase. This cannot be grasped by a stretched exponential function. This results in this small deviation from the analytical solution. For higher contact angle differences as shown in (a) and (b) the underlying approximations of the analytical solution become notable, but there is still a qualitative agreement.

IV. CONCLUSION

In this paper we characterized the dynamics of a droplet on a periodically switched surface via MD and TF simulations and the molecular kinetic theory of wetting. For this purpose, the MD and TF results were mapped spatially and temporally which shows a good agreement of both methods. Furthermore, we showed the applicability of MKT for wetting of switchable surfaces. Thus, we underlined that the scheme from de Ruijter, Blake, and De Coninck\textsuperscript{40} gives a useful tool to extract the required parameters for the molecular kinetic theory of wetting directly from MD simulations which can predict the contact angle changes while switching the wettability of a surface. Although for a more detailed description of wetting processes short time effects have to be included the results from MKT are highly similar with these obtained from MD simulations, which take some orders of magnitude more computational time and resources. The temporal evolution of the contact angle of a droplet on a switchable surface show just very small deviations if calculated with MD or MKT in the limit of small contact angle changes of $\sim 10^\circ$ but also is in good agreement for higher $\Delta \theta$. Under some approximations the MKT equation could be solved analytically yielding equations for properties like the plateau value and the amplitude of the temporal evolution of the contact angle of a droplet on a surface with oscillating wettability. Thus, it turned out that the plateau value of the contact angle depends on the period of switching. Here, the MKT method failed to indicate a minimum of these value for small periods seen in MD and TF simulations. This reflects the additional more complex short time dynamics of the contact angle at the beginning of each switching event.

The substrates in this work have been switched homogeneously. The control of pattern formation with the help of pre-structured substrates has been the focus of research in the past\textsuperscript{20,45}. 

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FIG. 8: (a) and (b) amplitudes resulting from stretched exponential fits to MD and TF data respectively for switching between $\varepsilon = 0.632$ and $\varepsilon = 0.762$. (c) and (d) amplitudes resulting from stretched exponential fits to MD and TF data respectively for switching between $\varepsilon = 0.632$ and $\varepsilon = 0.671$. The circles in (b) and (d) indicate the amplitude for the limit $T \to 0$, i.e. an effective wettability.

The combination of switchable, pre-structured substrates promises to offer even more detailed influence on the pattern formation and should be the focus of future work.

CONFLICTS OF INTEREST

There are no conflicts to declare.
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Appendix A: Calculation of the contact angle from rFWHM

For a spherical cap shaped droplet

\[ r^2 = \left( \frac{\sigma}{2} \right)^2 + \left( \frac{h}{2} - y_c \right)^2 \]  \tag{A1}

has to hold, where \( y_c = h - r \), \( h \) is the height and \( r \) the radius of the droplet and \( \sigma \) the width at half height. After some calculations we obtain

\[ r = \frac{1}{4h}(\sigma^2 + h^2). \]  \tag{A2}

Further, basic trigonometry yields

\[ \cos(\theta) = 1 - \frac{h}{r} \]  \tag{A3}

with the contact angle \( \theta \). By plugging Eq. (A2) into Eq. (A3) we get

\[ \cos(\theta) = 1 - \frac{h}{4h(\sigma^2 + h^2)} \]  \tag{A4}

and finally we obtain

\[ \cos(\theta) = 1 - \frac{4}{r_{FWHM}^2 + 1}. \]  \tag{A5}

Appendix B: Reformulation of MKT equation

The relation between the half chord length \( r \) and the half of the central angle \( \theta \) of a circular segment is given by

\[ r = \sqrt{2A} \frac{\sin(\theta)}{\sqrt{(2\theta - \sin(2\theta))}} = \sqrt{2A} f(\theta) \]  \tag{B1}

where \( A \) is the area of the circular segment. Here, \( r \) is the radius of a droplet on a surface and \( \theta \) 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{B2}

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{B3}

The MKT relation reads

\[ v = k_0(\cos(\theta_{eq}) - \cos(\theta)) \]  \tag{B4}
with \( k_0 = \frac{\gamma}{\xi} \) and can thus be rewritten as

\[
\frac{d}{dt} \cos(\theta) = -k_1 \frac{\sin(\theta)}{g(\theta)} (\cos(\theta_{eq}) - \cos(\theta)) \tag{B5}
\]

with \( k_1 = \frac{k_0}{\sqrt{2A}} \). As can be seen in Fig. 9 \( \frac{\sin(\theta)}{g(\theta)} \) can be approximated as \( 3(1 - \cos(\theta)) \). Thus, Eq. (B5) can be rewritten for intermediate changes in contact angles as

\[
\frac{d}{dt} \cos(\theta) = k_2 (1 - \cos(\theta)) (\cos(\theta_{eq}) - \cos(\theta)) \tag{B6}
\]

and for small changes as

\[
\frac{d}{dt} \cos(\theta) = k_3 (\cos(\theta_{eq}) - \cos(\theta)) \tag{B7}
\]

where \( k_3 = k_2 (1 - \cos(\theta_{eq})) \) since \( \cos(\theta) \) can be substituted by the constant \( \cos(\theta_{eq}) \). In Fig. 10 and 11 the two approximations and the solution from Eq. (B5) are plotted for a single switching event and periodic switching.
FIG. 10: $\cos(\theta)$ plotted versus $t$ for the different approximations of the MKT for (a) a single switch and (b) periodic switching between $\varepsilon_w = 0.40$ and $\varepsilon_w = 0.45$.

FIG. 11: $\cos(\theta)$ plotted versus $t$ for the different approximations of the MKT for (a) a single switch and (b) periodic switching between $\varepsilon_w = 0.40$ and $\varepsilon_w = 0.58$.

From Eq. (B6) on after separation of variables one can write

$$
\frac{dx}{(1-x)(x-x_{eq})} = -k_2 dt \quad \text{(B8)}
$$

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

$$
\frac{1}{(1-x)(x-x_{eq})} = \frac{1}{1-x_{eq}} \left[ \frac{1}{1-x} + \frac{1}{x-x_{eq}} \right] \quad \text{(B9)}
$$
Therefore, one obtains for the solution of the differential equation

\[ -\ln(1-x) + \ln(x-x_{eq}) = -k_2(1-x_{eq})t + C \]  \hspace{1cm} (B10)

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

\[ \frac{x-x_{eq}}{1-x} = \frac{x_0-x_{eq}}{1-x_0} \exp(-k_3 t) \]  \hspace{1cm} (B11)

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

\[ x(t) = \frac{x_{eq} + \varepsilon(t)}{1 + \varepsilon(t)} \]  \hspace{1cm} (B12)

with

\[ \varepsilon(t) = \frac{x_0-x_{eq}}{1-x_0} \exp(-k_3 t) \]  \hspace{1cm} (B13)

This could be analysed numerically (e.g. fitting by stretched exponentials). However, it is possible to rewrite this function 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 \( \varepsilon^2 \). This yields

\[ x(t) = [x_{eq} + \varepsilon(t)][1 - \varepsilon(t) + \varepsilon(t)^2 + ...] \approx x_{eq} + (1-x_{eq})(\varepsilon(t) - \varepsilon(t)^2) + ... \]  \hspace{1cm} (B14)

Now we introduce the normalized relaxation function

\[ y(t) = \frac{x(t) - x_{eq}}{x_0-x_{eq}} \]  \hspace{1cm} (B15)

Then we may write

\[ y(t) = \frac{1-x_{eq}}{1-x_0} \left[ \exp(-k_3 t) - \frac{x_0-x_{eq}}{1-x_0} \exp(-2k_3 t) \right] \]  \hspace{1cm} (B16)

**Appendix C: Analytical calculation**

We start from Eq. (18) with a contact angle independent \( k_i \):

\[ \frac{d}{dt} y(t) = -k_{3,i} (y - a_i) \]  \hspace{1cm} (C1)

Its general solution reads

\[ y(t) = a_i (1 - e^{-k_{3,i} t}) + y(0) e^{-k_{3,i} t} \]  \hspace{1cm} (C2)
Here, 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 \(T\). As before, \(y\) is a normalized version of the cosine of the contact angle. Thus, for the first half switching period one obtains
\[
y(t) = y(0) \exp(-k_3 \downarrow t)
\] (C3)
and for the second half
\[
y(t) = (1 - \exp(-k_3 \uparrow t)) + y(0) \exp(-k_3 \downarrow T/2) \exp(-k_3 \uparrow T/2)
\] (C4)

The average over the first time interval is given by
\[
\langle y_1 \rangle = y(0) \frac{1}{k_3 \downarrow T/2} (1 - e^{-k_3 \downarrow T/2})
\] (C5)
and that over the second time interval
\[
\langle y_2 \rangle = 1 - \frac{1 - \exp(-k_3 \uparrow T/2)}{k_3 \uparrow T/2} + y(0) \exp(-k_3 \downarrow T/2) \frac{1}{k_3 \downarrow T/2} (1 - e^{-k_3 \downarrow T/2})
\] (C6)
\[
= 1 - \frac{(1 - e^{-k_3 \uparrow T/2})}{k_3 \uparrow T/2} (1 - y(0) \exp(-k_3 \downarrow T/2))
\] (C6)

The average over both time intervals finally reads
\[
\langle y(0) \rangle = \frac{1}{2} - \frac{1 - \exp(-k_3 \uparrow T/2)}{2k_3 \uparrow T/2} + y(0) \left[ \frac{1}{2k_3 \downarrow T/2} (1 - e^{-k_3 \downarrow T/2})
\right.
\[
+ e^{-k_3 \downarrow T/2} \frac{1}{2k_3 \downarrow T/2} (1 - e^{-k_3 \uparrow T/2}) \right]
\] (C7)

Next, we define \(y(n)\) as the value of \(y\) after \(n\) full periods, i.e. at time \(t = 2nT/2\). Naturally, Eq. (C7) can be generalized to express the average \(y(n)\) during the time \(t = 2nT/2\) and \(t = 2(n+1)T/2\) in dependence of \(y(n)\). 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 \(K_3 = k_3 \downarrow + k_3 \uparrow\))
\[
y(1) = (1 - \exp(-k_3 \uparrow T/2)) + y(0) \exp(-KT/2) \equiv C + Dy(0)
\] (C8)

In general one has
\[
y(n) = C + Dy(n - 1)
\] (C9)

This recursive relation has a straightforward solution which reads (setting \(y(0) = 1\))
\[
y(n) = C(1 + D + D^2 + \ldots + D^{n-1}) + D^n = C \frac{1 - D^n}{1 - D} + D^n
\] (C10)
\[
= \frac{1 - \exp(-k_3 \uparrow T/2)}{1 - \exp(-K_3 T/2)} (1 - e^{-K_3 nT/2}) + e^{-K_3 nT/2}
\]
Thus, we finally have
\[
\langle y(n) \rangle = \frac{1}{2} - \frac{1 - \exp(-k_{3,\uparrow}T/2)}{2k_{3,\uparrow}T/2} \\
+ \left[ \frac{1 - \exp(-k_{3,\uparrow}T/2)}{1 - \exp(-K_{3}T/2)} \left( 1 - e^{-K_{3}nT/2} + e^{-K_{3}nT/2} \right) \right] \\
+ \left[ \frac{1}{2k_{3,\downarrow}T/2} \left( 1 - e^{-k_{3,\downarrow}T/2} \right) + e^{-k_{3,\downarrow}T/2} \frac{1}{2k_{3,\uparrow}T/2} \left( 1 - e^{-k_{3,\uparrow}T/2} \right) \right]
\]
(C11)

In the long-time limit one finds the plateau value
\[
\lim_{n \to \infty} y(n) = \frac{1}{2} \left\{ 1 + \frac{1 - \exp(-k_{3,\uparrow}T/2)}{1 - \exp(-K_{3}T/2)} \frac{1}{k_{3,\uparrow}T/2} \left( 1 - e^{-k_{3,\downarrow}T/2} \right) \right\} \\
- \frac{1 - \exp(-k_{3,\downarrow}T/2)}{k_{3,\downarrow}T/2} \left( 1 - \frac{1 - \exp(-k_{3,\uparrow}T/2)}{1 - \exp(-K_{3}T/2)} e^{-k_{3,\downarrow}T/2} \right) \right\} \\
= \frac{1}{2} \left\{ 1 + \frac{1 - \exp(-k_{3,\uparrow}T/2)}{1 - \exp(-K_{3}T/2)} \frac{1}{k_{3,\downarrow}T/2} \left( 1 - e^{-k_{3,\downarrow}T/2} \right) \right\} \\
- \frac{1}{k_{3,\downarrow}T/2} \right\} \equiv y_{\text{plateau}}
\]
(C12)

For very fast switching this boils down to
\[
y_{\infty} = \frac{k_{3,\downarrow}}{k_{3,\downarrow} + k_{3,\uparrow}} - \frac{k_{3,\uparrow} - k_{3,\downarrow}}{24(k_{3,\downarrow} + k_{3,\uparrow})} k_{3,\downarrow} k_{3,\uparrow} (T/2)^{2}
\]
(C13)

The general equation for \( y(n) \) can be rewritten with \( y_{\text{plateau}} \)
\[
\langle y(n) \rangle = y_{\text{plateau}} \pm \exp(-K_{3}nT/2) \left( 1 - \frac{1 - \exp(-k_{3,\uparrow}T/2)}{1 - \exp(-K_{3}T/2)} \right) \\
+ \left[ \frac{1}{2k_{3,\downarrow}T/2} \left( 1 - e^{-k_{3,\downarrow}T/2} \right) + e^{-k_{3,\downarrow}T/2} \frac{1}{2k_{3,\uparrow}T/2} \left( 1 - e^{-k_{3,\uparrow}T/2} \right) \right] \\
= y_{\text{plateau}} \pm e^{-K_{3}(n + \frac{1}{2})T/2} e^{K_{3}T/2} \frac{1}{1 - \exp(-K_{3}T/2)} \\
+ \left[ \frac{1}{2k_{3,\downarrow}T/2} \left( 1 - e^{-k_{3,\downarrow}T/2} \right) + e^{-k_{3,\downarrow}T/2} \frac{1}{2k_{3,\uparrow}T/2} \left( 1 - e^{-k_{3,\uparrow}T/2} \right) \right] \\
\equiv y_{\text{plateau}} \pm e^{-K(n + \frac{1}{2})T/2} \hat{y}
\]
(C14)
The ± distinguishes an initial higher wettability (+) from an initial lower wettability (−). Due to the inherent symmetry exchanging $k_{3,\downarrow}$ with $k_{3,\uparrow}$ and vice versa gives the relation for an initial lower wettability. For $k_{3,\downarrow} = k_{3,\uparrow} = k_3$ this can be rewritten as

$$y(n) = \frac{1}{2} + e^{-k_3(2n+1)T/2} \frac{1 - \exp(-k_3T/2)}{1 - \exp(-2k_3T/2)} \frac{1}{2k_3T/2}$$

$$+ (1 - \exp(-k_3T/2))(1 + \exp(-k_3T/2))$$

$$= \frac{1}{2} + \exp(-k_3(2n+1)T/2) \frac{1}{2k_3T/2} (1 - \exp(-k_3T/2))$$

(Appendix D: $\zeta$)

Table Tab. II shows values of $\zeta$ extracted from the MD model with two different methods. $\zeta$ 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. $\zeta_{fit}$ denotes the $\zeta$ value extracted from an analysis of the contact line velocity in dependence of the cosine of the contact angle. A visualisation is shown in Figure 2.

**TABLE II:** Values of $K_0$, $n$, and $\zeta$ directly calculated from MD simulations as well as values of $\zeta_{fit}$ extracted from the analysis of the contact line velocity dependence on the cosine of the contact angle.

| $\varepsilon$ | $K_0/\tau^{-1}$ | $n/\sigma^{-3}$ | $\zeta_{MD}$ |
|---------------|-----------------|-----------------|--------------|
| 0.447         | $4.62 \cdot 10^{-4}$ | 0.57            | 0.93 $\cdot 10^3$ |
| 0.548         | $3.81 \cdot 10^{-4}$ | 0.62            | 1.23 $\cdot 10^3$ |
| 0.632         | $3.24 \cdot 10^{-4}$ | 0.66            | 1.53 $\cdot 10^3$ |
| 0.707         | $2.76 \cdot 10^{-4}$ | 0.69            | 1.88 $\cdot 10^3$ |
| 0.742         | $2.55 \cdot 10^{-4}$ | 0.70            | 2.07 $\cdot 10^3$ |
| 0.762         | $2.44 \cdot 10^{-4}$ | 0.71            | 2.19 $\cdot 10^3$ |
| 0.809         | $2.40 \cdot 10^{-4}$ | 0.71            | 2.23 $\cdot 10^3$ |
| 0.775         | $2.17 \cdot 10^{-4}$ | 0.73            | 2.51 $\cdot 10^3$ |
| 0.837         | $2.03 \cdot 10^{-4}$ | 0.74            | 2.73 $\cdot 10^3$ |

In the TF model the contact angle velocity can be analyzed analogously. The resulting values can be found in Tab. III.
TABLE III: Values of $\zeta$ within the TF model extracted from the analysis of the contact line velocity dependence on the cosine of the contact angle

| Initial $\epsilon$ | Final $\epsilon$ | $\zeta_{fit}$ |
|--------------------|------------------|--------------|
| 0.762              | 0.632            | 1.04         |
| 0.671              | 0.632            | 1.10         |
| 0.632              | 0.671            | 1.24         |
| 0.632              | 0.762            | 1.72         |

Appendix E: Stretching/compression of the relaxation

We have identified the average relaxation time $\langle \tau \rangle$ with the expression in Eq. (15). Additionally, we can define the $n$-th moment of $y(t)$ as

$$
\langle \tau^n \rangle = \frac{\int_0^\infty t \cdot y(t) dt}{\int_0^\infty y(t) dt}.
$$

Now, we can compute the quantity

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

which is equal to one for a pure exponential function $y(t)$. If this quantity is greater than 1, it implies a compressed exponential function, i.e. $\beta > 1$. And if the expression in Eq. (E2) is smaller 1, it implies a stretched exponential function, i.e. $\beta < 1$.

TABLE IV: Values of $\beta$ obtained from an stretched exponential fit to the data for a single switching event from $\epsilon_1$ to $\epsilon_2$ in MD, MKT and TF simulations.

| $\epsilon_1$ | $\epsilon_2$ | $\beta_{MD}$ | $\beta_{MKT}$ | $\beta_{TF}$ |
|---------------|---------------|--------------|---------------|--------------|
| 0.632         | 0.762         | 0.87         | 0.73          | 0.68         |
| 0.762         | 0.632         | 1.68         | 1.42          | 2.05         |

For the $y(t)$ given in Eq. (14) we get

$$
\frac{\langle \tau^2 \rangle}{2\langle \tau \rangle^2} = \frac{(1 - \frac{B}{8})(1 - \frac{B}{2})}{(1 - \frac{B}{4})^2} = \frac{1 - \frac{5}{8}B + \frac{B^2}{16}}{1 - \frac{1}{2}B + \frac{B^2}{16}},
$$

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. (E3) has to be smaller than 1 and finally $\beta$ 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, which are shown in Tab. IV.

**Appendix F: Additional plots of the contact line velocity $v_{cl}$ versus $\cos(\theta)$**

Figures 12, 13, 14 and 15 show the contact line velocity dependence on the cosine of the contact angle for additional wettabilities not discussed in main manuscript.

**FIG. 12: Contact line velocity $v_{cl}$ plotted against $\cos(\theta)$ for switching between wettabilities of $\varepsilon_{LW} = 0.25$ and $\varepsilon_{HW} = 0.30$.**
FIG. 13: Contact line velocity $v_{cl}$ plotted against $\cos(\theta)$ for switching between wettabilities of $\varepsilon_{LW} = 0.30$ and $\varepsilon_{HW} = 0.35$.

FIG. 14: Contact line velocity $v_{cl}$ plotted against $\cos(\theta)$ for switching between wettabilities of $\varepsilon_{LW} = 0.35$ and $\varepsilon_{HW} = 0.40$. 
FIG. 15: Contact line velocity $v_{cl}$ plotted against $\cos(\theta)$ for switching between wettability of $\varepsilon_{LW} = 0.40$ and $\varepsilon_{HW} = 0.45$.

Appendix G: Stretched exponential fits

Figure 16 shows how the stretched exponential functions match the data they were fitted to for the TF model. Figure 17 shows the agreement of the stretched exponential functions to the simulation data for the MKT and the MD model.
FIG. 16: 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) $0.40 \rightarrow 0.45$, b) $0.45 \rightarrow 0.40$, c) $0.40 \rightarrow 0.58$ and d) $0.58 \rightarrow 0.40$. 
FIG. 17: 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) $0.40 \leftrightarrow 0.45$ (MKT), (b) $0.40 \leftrightarrow 0.45$ (MD), (c) $0.40 \leftrightarrow 0.58$ (MKT) and (d) $0.58 \leftrightarrow 0.40$ (MD).
Appendix H: Minimum $y_{plateau}$ value

![Diagram](image)

**FIG. 18:** (a) $\cos(\theta)_{plateau}$ obtained from MD, MKT, MKT with short time effects (MKT_st), TF and from Eq. (20) 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. 18 after each switching event the value of $\zeta_{MD}$ was scaled with a factor of $-50$ for 1500 time steps when switching to a higher wettability and $\frac{3}{5} \cdot 1500$ time steps when switching to the lower wettability. The factor of $\frac{3}{5}$ results from the relation of the time steps that show the nonlinear behavior in Fig. 3. This qualitative result demonstrates that the MKT can be adapted to incorporate short time effects.