



Molecular Processes in Dynamic Wetting

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ABSTRACT

The spreading of liquids onto and over surfaces is a fundamental process in nature. It is present in all forms and sizes: From rivers carving through landscapes, to our blood stream transporting nutrients to cells, and even single water molecules moving through channels into these cells. We now have a good understanding of how fluid movement works inside the fluid itself. However, we do not fully understand the processes close to the contact line, where the liquid is spreading onto the surface. We are forced to make assumptions about this behaviour and none of these assumptions have yet proven to be universally valid.

As everything in nature, liquid spreading is a fundamentally molecular process. This thesis summarises my work on applying this lens to the process. By studying molecules we begin at the smallest combined building blocks of nature and do not have to make any prior assumptions of the involved processes. Instead, we simply observe their behaviour. This is accomplished through the use of molecular dynamics simulation, which are an atomistic form of computer experiments. We use a realistic model of water molecules as our base liquid, since this captures realistic effects such as hydrogen bonding which are not present when using simpler models. Combined with large-scale systems which minimise the influence of finite-size effects, we have a realistic treatment of complex liquid systems.

We find that the molecular processes of wetting have an important influence on large-scale wetting. Most importantly, the hydrogen bonding nature of water to realistic substrates yields the no-slip condition often used as a boundary condition for models of wetting. Furthermore, since molecular processes are thermal in nature they create energy barriers which impede contact line advancement. We show how these barriers are created and how they can be diminished, for example in the case of electrowetting. This highlights that understanding the molecular behaviour of fluids remains an important field of study.

KEYWORDS contact lines, nanodroplets, computational physics, molecular dynamics, fluid dynamics, multi-phase flows, electrowetting

SAMMANFATTNING

Hur vätskor breder ut sig över ytor är en grundläggande process i naturen. Den dyker upp i alla former och storleksgrader: från floder som skär genom berg, till vår blodström som levererar näring till våra celler, och till och med enstaka vattenmolekyler som rör sig genom de kanaler som celler tar in näringen från. Hur vätskor betar sig i stora flöden är sedan länge känt, men vi vet ännu inte hur de betar sig nära ytor. Istället gör vi antaganden, varav inga ännu är korrekta för alla tillämpningar.

Fundamentalt sett är en vätska som breder ut sig en molekyllär process. Denna avhandling sammanfattar mitt arbete med att förstå den ur denna synvinkel. Genom att studera molekyler använder vi naturens minsta sammansatta byggstenar. Vi behöver inte göra antaganden om hur de betar sig, vi behöver bara titta. Det fönster som vi tittar igenom är molekyllär dynamik-simuleringar, en atomistisk typ av datorexperiment. För att fånga verkliga effekter som vätebindningar, använder vi realistiska modeller av vattenmolekyler och ytor. Vi använder tillräckligt stora system för att se hur molekyllära effekter påverkar större processer.

Vi visar med dessa metoder att molekyllära processer har stor påverkan på hur vätskor flödar över ytor. En stor effekt är att vätebindningarna mellan vatten och realistiska ytor förhindrar vätskan från att glida över den, vilket är ett vanligt antagande i modeller. Vi visar också hur molekyler vid gränsen där vätskor sprider på ytor ger upphov till en energibarriär som förhindrar att vätskan enkelt sprider sig framåt. Denna barriär beskrivs i detalj och vi visar vilka effekter som kan förminska den. Detta genomlyser hur molekyllära processer i vätnings är en viktig ingrediens för ökad förståelse av vätskespridning i system.

List of publications

Paper I Petter Johansson, Andreas Carlson, and Berk Hess (2015). “Water-substrate physico-chemistry in wetting dynamics”. *Journal of Fluid Mechanics* 781, pp. 695–711.

Paper II Petter Johansson and Berk Hess (2018). “Molecular origin of contact line friction in dynamic wetting”. *Physical Review Fluids* 3, p. 074201.

Paper III Uģis Lācis, Petter Johansson, Tomas Fullana, Berk Hess, Gustav Amberg, Shervin Bagheri, and Stéphane Zaleski (2019). “Steady moving contact line of water over a no-slip substrate”. Submitted to European Physical Journal Special Topics.

Paper IV Petter Johansson and Berk Hess (2019). *Electrowetting diminishes contact line friction in molecular wetting*. Submitted to Physical Review Fluids. arXiv: 1912.09042.

Author contributions

I AC and BH initiated the project. BH developed the molecular dynamics (MD) simulation methods. AC performed the phase-field simulations. PJ developed the MD analysis tools and performed the droplet simulations. All authors participated in the analysis. PJ and BH wrote the initial draft.

- II* PJ and BH initiated the project. PJ constructed the MD systems and performed the simulations. BH developed the friction model. Both authors participated in the analysis. PJ wrote the initial draft.
- III* The project was jointly initiated by UL, BH, GA, SB and SZ. PJ performed the MD simulations, UL the PF simulations and TF the VOF simulations. All authors contributed to analysis and discussions concerning the project. UL, PJ, TF and SZ wrote the initial draft with feedback from the remaining authors.
- IV* PJ and BH initiated the project. PJ constructed the MD systems and performed the simulations. PJ developed the analysis tools and both authors participated in the analysis. PJ wrote the initial draft.

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Introduction

CHAPTER ONE

Look out of your window on a rainy day and think of water droplets hitting the glass. Stand too close to a dog shaking its fur after a bath and feel how they spread into your clothes. Or imagine a droplet hanging from a dew catcher, sitting on a leaf, or skidding around in a hot frying pan. Water is crucial to all forms of life on earth and droplets spreading onto or into surfaces is a common sight.

The flow of fluids has also inspired a wealth of technical applications. Rushing water generates power by turning turbines, or is used to cool large systems. But fluids are not only useful in large amounts. Inkjet printer heads shoot microscopic droplets at high speeds onto paper and spray cooling can be used to cool mechanical parts. There is also a growing interest in biological and medicinal use of microscopic flows. These use the inherent properties of fluids and small channels to create cheap, portable and low-power diagnostic devices.

The study and development of these applications form the developing

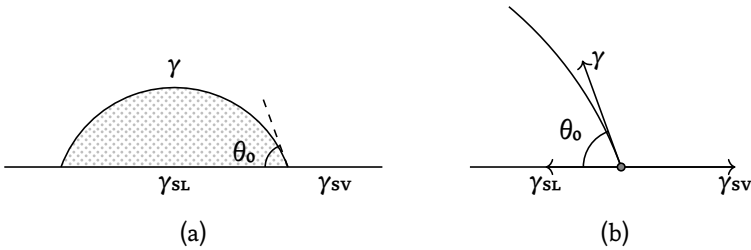


FIGURE 1.1 A droplet spreads out to form a spherical cap with the angle θ_0 at the triple contact line (a). The equilibrium depends on the surface tension force balance (b).

field of *microfluidics*. Some claim that it may turn out to be as important a field in this century as the development of the microprocessor was in the last. However, getting to that point still demands that many issues are resolved.

1.1 Static and dynamic wetting

A droplet sitting on a surface is in an equilibrium state. Our knowledge of thermodynamics informs us that these static states depend on the energy of the system. A droplet is formed because its constituent atoms decrease their potential energy by being close together, forming bonds.

A material's—liquid, gas, or solid—tendency to stay together is measured by its *surface tension*. A high surface tension means that it takes a lot of energy to expand the material's exposed surface. An example of this in nature is how certain insects can walk on water. Regular water has a relatively high surface tension[†] and prefers to stick to itself over to their legs. This results in a buoyant force which overcomes the effect of gravity pulling the critters downwards.

Nature also shows us that droplets form in different ways on different surfaces. Perhaps most memorable is how water placed on lotus leaves forms almost spherical pearls, while they will typically appear half-spher-

[†]Owing to the water molecules forming *hydrogen bonds* with each other. We will discuss these bonds in more detail in chapter 2.

ical on most other surfaces. In the early 1800s, Thomas Young realised that whenever a liquid contacts another component there is a competition between the two to simultaneously minimise their individually costly surfaces. This competition leads to the droplet spreading out on—or, wetting—the surface, as shown in figure 1.1. This realisation led to a relationship between the surface energies of the involved phases and the equilibrium state of the droplet (Young 1805):

$$\gamma \cos \theta_0 = \gamma_{sv} - \gamma_{sl} \quad (1.1)$$

where γ_{sv} is the surface tension of the solid and surrounding vapour interface, γ_{sl} that of the solid and liquid interface and θ_0 the angle that is made at the point where the phases meet. γ is the surface tension of the liquid and vapour interface but is generally just referred to as the surface tension of the liquid itself. This relationship is referred to as *Young's equation* and the angle θ_0 as the equilibrium contact angle, or simply the Young angle.

While equation (1.1) fully describes how droplets will end up resting on surfaces, it tells us nothing of what happens as they are reaching that final state. Imagine a droplet being placed on a plate. What does it look like while it is spreading out? How long does it take until it is finished? How can we make this process as efficient as possible? Simple questions, yet important to answer.

These processes and the study thereof is collectively known as *dynamic wetting*. For more than fifty years there has been a lot of activity in this field. From an industrial view due to wanting to process liquids at ever more rapid paces, in academia due to not yet understanding it on a fundamental level. Problems stem from how liquid transport is a complicated phenomena spanning length scales from millimetre sized movement all the way down to molecular processes.

In this thesis we study how the nature of individual water molecules influence liquid spreading. Since we cannot observe molecular motions in laboratory experiments we instead use large scale computer simulations of realistic systems to probe this influence. These methods are described in chapter 2. In chapter 3 we present the results of these droplet experiments.

These are compared to different theoretical models of wetting and a model for how the contact line advances is proposed. Finally, chapter 4 presents a more advanced study of electrowetting using our molecular systems and relates our findings to modern laboratory experiments.

Computer simulations of droplets

CHAPTER TWO

Studying a droplet spreading on a substrate is in principle very easy: simply set up a camera beside a plate, then use a pipette to place a droplet onto the plate and record the process. In practice it is more difficult, since you may need multiple cameras and a way to account for how light refracts through liquids to obtain accurate results. Nevertheless, researchers have over the years worked to perfect these measurements and by now best practices are well established.

There are however limits to what regular lab experiments can study. As systems become smaller, so does the time for every finished experiment decrease. This places extraordinary demands on capturing equipment, which has to be both high-speed and high-resolution. There is also a more fundamental problem, in that cameras cannot capture detailed molecular behaviour, only their collective motions.

We can solve these issues by performing our experiments as computer simulations. In a computer we can create an experiment that is as small

as we require. Most importantly, with certain types of simulations we can observe the behaviour and impact of individual molecules on our experiment. The most common method of that type is *molecular dynamics* (MD) simulations.

2.1 Molecular dynamics simulations

The goal of any computer simulation—or, experiment—is to correspond to physical reality. The laws of physics are enforced through the model we use to perform the experiment with. The model is in turn selected to suit our experiment. A computer game might need Newton’s laws to make apples fall to the ground when dropped, while a simulated ocean in a movie would evolve using the Navier–Stokes equations of hydrodynamics, and a research simulation of a plasma requires a treatment of flowing electrical charges.

Similarly, we select how detailed (granular) our simulation has to be depending on our requirements. An astronomer modelling how a galaxy will evolve over thousands of years will only have to consider entire star systems as individual elements. A quantum physicist on the other hand will have to consider the influence of individual electrons to accurately capture the physics of a small group of molecules, but can ignore that an entire universe exists just a small distance away from them.

Molecular dynamics has been developed to study the behaviour of systems consisting of downwards of hundreds of atoms. As such it typically includes every atom as a separate entity in the simulation[†] and uses classical Newtonian mechanics to move them around in small time steps of size Δt .

This is fundamentally an incorrect view of atomic movement. Quantum mechanics has proven that a particle’s position and velocity cannot be perfectly known at the same time and that energy is quantised. But by

[†]A specific class of MD simulations exists wherein some atom groups are treated as a single atom. These are referred to as being *coarse-grained* and are used to perform longer or larger simulations which would be infeasible with an all-atom treatment.

studying a large set of particles we minimise the influence of single errors. Quantum mechanical phenomena are added in a simplified sense by tuning the forces through which particles interact with each other.

Combined, while an MD simulation does not perfectly model atomic phenomena, it should capture the aggregate behaviour of the entire system. In essence, we trade a perfect model of atomic movement for one which is merely good enough. In return, the simpler physical models allow MD simulations to be used for larger systems for longer times than a quantum mechanical simulation can.

This flexibility has made MD popular for many scientific fields whose typical systems consist of between hundreds and millions of individual atoms. A few examples include biophysics, where MD is often used to study how drugs or toxins affect how signals are transmitted to human cells through atomic channels, structural mechanics which wants to understand how materials behave during extreme stresses, and of course fluid mechanics, which this thesis will cover in more detail.

A full description of molecular dynamics is outside of the scope of this thesis. The rest of this section will introduce the basic foundations of the method. More in depth information has been collected by among others Allen and Tildesley (1987), Frenkel and Smit (2002), Berendsen (2007) or can be found in the Gromacs user manual (Lindahl et al. 2020). Simulations discussed in this thesis have been performed using the Gromacs molecular dynamics software package (Abraham et al. 2015; Páll et al. 2015).

Interactions between atoms

A crucial part of describing atomic movement in a system is knowing how they interact with each other. In Newtonian mechanics movement of an object with mass m follows from the force $\vec{F} = m\vec{a}$, where \vec{a} is the resulting acceleration. The arrow (\rightarrow) is used to denote a 3-component vector, since particles are moving in our familiar three-dimensional space.

The force is generated by a system wanting to minimise its potential energy U . A particle will want to move in the direction of where U decreases most. This is expressed using the gradient

$$\vec{F} = -\nabla U \quad (2.1)$$

for the nabla operator

$$\nabla = \frac{\partial}{\partial x} \hat{x} + \frac{\partial}{\partial y} \hat{y} + \frac{\partial}{\partial z} \hat{z} \quad (2.2)$$

where a hat (^) denotes a unit vector.

The short of it then is that to determine the force acting on an atom in our simulation, we need to know its potential energy (or rather, the slope of it). We can decompose contributions to the potential into different categories: a) bonded interactions with other atoms, b) non-bonded interactions with other atoms, c) constraints that are applied on the atom, and d) external contributions, for example from an electric field.

Constraints and external contributions are typically added on an as-required basis when creating a simulation system. The bonded and non-bonded interactions are more general since they involve atoms interacting with each other. They are discussed below.

Bonded interactions

Atomic bonds keep molecules in certain configurations. Either to keep two atoms i and j at a specified distance d_{ij} from each other or to have three atoms i , j and k form an angle α_{ijk} between themselves[†]. For both types a simple harmonic potential is commonly, but not exclusively, used. With those, the contribution for atom i is

$$U_{i,\text{bonded}} = \sum_j \frac{k_{ij}(r_{ij} - d_{ij})^2}{2} + \sum_{j,k} \frac{\kappa_{ijk}(\varphi_{ijk} - \alpha_{ijk})^2}{2} \quad (2.3)$$

where the first sum is over all of its distance bonds and the second over its angular. r_{ij} and φ_{ijk} are respectively the *current* distances and angles for the

[†]Four-point *dihedral interactions* are also commonly considered, but ignored here for the sake of simplicity and because they are not used in this thesis. Similar to keeping a constant angle between two atoms, they keep a constant angle between two planes.

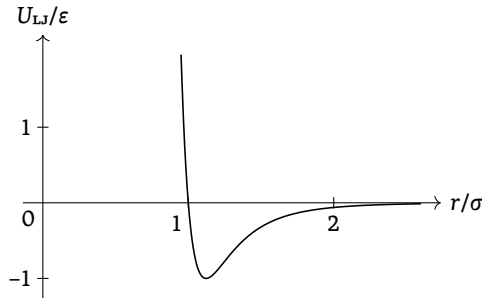


FIGURE 2.1 Lennard-Jones potential for an atomic species with parameters σ and ϵ .

bonded atom pairings. k_{ij} and κ_{ijk} are the corresponding spring coefficients determining how rigid the bonds are.

Non-bonded interactions

Atoms can interact with each other over some distance, not just through bonds. These non-bonded interactions[§] fall into three types: an extremely short-ranged repulsive potential which keeps atoms from occupying the same space, a weak attractive potential which brings neutral atoms together, and a Coulomb interaction between charged particles.

In computer simulations the repulsive and attractive parts are usually modelled by the Lennard-Jones potential

$$U_{LJ} = \frac{C_{12}}{r^{12}} - \frac{C_6}{r^6} \quad (2.4)$$

$$C_6 = 4\epsilon\sigma^6$$

$$C_{12} = 4\epsilon\sigma^{12}$$

which is shown in figure 2.1. r is the distance between two atoms, ϵ sets the strength of the interaction potential and σ adjusts the potential minima position. These latter two *Lennard-Jones parameters* are set individually for each atomic species i . For the interaction with a different atomic species

[§]Also commonly known as *van der Waals interactions*.

j they are either set explicitly to model some (usually experimental) behaviour, or calculated using a combination rule. For the popular Lorentz-Berthelot rules the combined parameters are

$$\begin{aligned}\sigma_{ij} &= \frac{\sigma_i + \sigma_j}{2} \\ \varepsilon_{ij} &= \sqrt{\varepsilon_i \varepsilon_j}\end{aligned}\tag{2.5}$$

but other variants exist.

The Coulomb interaction potential for two particles with charges q_i and q_j at a distance r from each other is

$$U_{\text{coulomb}} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r^2}\tag{2.6}$$

where ε_0 is the permittivity in vacuum.

To determine the full non-bonded interaction potential for an atom the contributions from all other atoms in the system are added up. This is in contrast to the bonded potential calculation in (2.3), where only the closest atoms will contribute. If we are simulating a system with a number of atoms N , every atom has to calculate its potential with the $N-1$ other atoms. In computational terms this is called an N^2 complexity problem: the number of calculations is proportional to the number of elements squared.

This computational cost would quickly become too high for any large system, but there are ways to decrease it. Since the Lennard-Jones potential quickly approaches zero as the distance r increases it can be cut at some distance r_c , often at $r_c = 3\sigma$, which means that we only have to include a relatively small number of interactions around each atom. Coulomb interactions cannot similarly be ignored at some distance, but a popular method called *particle mesh Ewald* (PME) has been developed which performs the long-distance sum in Fourier space (Essmann et al. 1995). This improves the scaling from N^2 to $N \log N$.

Non-bonded interactions are by far the most costly calculation in MD simulations. Modern work, including but not limited to the above methods, have allowed larger systems to be simulated, but it is still the largest limiting factor of increasing the system size.

Force fields

In discussing the different types of interactions, quite a few parameters have been introduced. These parameters are often collected for different atomic species to replicate some desired real world behaviour. These collections of atomic parameters—most importantly the Lennard-Jones parameters σ , ϵ , charges q and atom masses m —are called *force fields*.

An important feature to keep in mind is that they are not universal: they are developed to match experiments in specific conditions and for specific parameters like the Lennard-Jones cutoff r_c and combination rules.

Updating the movement

With the force \vec{F} calculated for all atoms their positions \vec{r} and velocities \vec{v} can be updated. This is done using an *integrator*, which is a set of instructions for doing the update with minimal error. A popular one is the *leap-frog integrator*, which keeps the positions at time t and the velocities at time $t - \Delta t/2$ where Δt is the difference in time between two steps of the simulation. The update is then done in two steps:

$$\begin{aligned}\vec{v}(t + \Delta t/2) &= \vec{v}(t - \Delta t/2) + \frac{\vec{F}(t)}{m} \Delta t \\ \vec{r}(t + \Delta t) &= \vec{r}(t) + \vec{v}(t + \Delta t/2) \Delta t\end{aligned}\tag{2.7}$$

This integration conserves the system energy and is fully time-reversible, both of which are essential features in molecular simulations.

Periodic boundaries

Systems are generally not simulated inside an infinite vacuum, but in a simulation box of some size. So, what happens if a molecule moves outside of this box? This is often not desired. If, for example, we are simulating a gas we do not want it to spread out infinitely, but stay inside the box to keep a fixed pressure.

This is done by our boundary condition and the most commonly used in MD simulations is the *periodic boundary condition* (PBC). With PBCs we

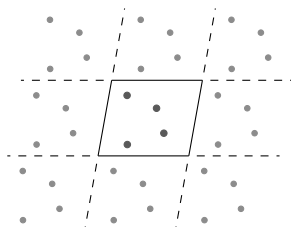


FIGURE 2.2 Two-dimensional view of the periodic boundary condition, which replicates the system infinitely along each axis.

simply replicate the system box around the system as shown in figure 2.2. As an atom leaves the system at one side, it is moved to the opposite side. All atoms also interact with atoms in the infinite periodic images, which is where the methods of cutting the Lennard-Jones potential and using PME for the Coulomb interactions come in handy.

Another boundary condition used in this thesis is the *reflecting condition*. This is a simple wall which stops atoms from leaving the box, for example the strongly repulsive $1/r^{12}$ term from the Lennard-Jones potential (2.4).

Limitations

Molecular dynamics simulations are a powerful tool but one has to keep in mind in which ways they can fail. Most important is that while the simulations themselves are *ab initio*—evolve through the laws of physics without the need for boundary conditions—they still rely on sensible setups. Force fields must be constructed to reflect reality, or at least a desired aspect of it. Since MD uses classical physics quantum effects can only be described in an aggregate way through the force field⁹. The force field includes the electron cloud around molecules as a simplified and static factor. Likewise, intermolecular bonds are typically fixed and cannot be broken.

⁹A hybrid approach exists in quantum mechanics/molecular mechanics (QM/MM) methods. In this method a quantum mechanical model is used for specific regimes and blended with simpler models for speed (Warshel and Levitt 1976).

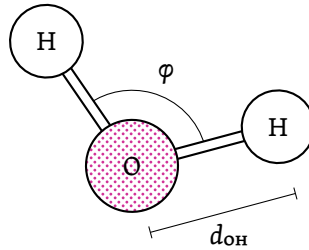


FIGURE 2.3 Geometry of a water molecule.

These limitations are generally not a problem for simulations. Aggregate behaviour is conserved when sampling sufficiently large systems or long simulation times. However, purely quantum mechanical components like electric conductors, wherein electrons move freely and more or less instantaneously, cannot be simulated using molecular dynamics. In such cases desired quantum effects have to be included as a boundary condition.

Conversely, since MD is good at describing aggregate behaviour larger scale systems can be accurately simulated. Caveat being that the computational cost increases with the system size and that supercomputers cannot perfectly scale to more computational processes without inefficiency losses.

In total then, MD is limited in the smaller end of the size spectra by not accurately describing atomic and quantum mechanical effects. In the larger end by the computational cost and limits of available computational power. MD then, is developed to work in between these scales. It excels in the mesoscopic regime, where molecular and continuum physics blend.

2.2 Simulating water

The simple and beautiful water molecule consists of three atoms: one oxygen atom, onto which two hydrogen atoms are bound. In a classical model, shown in figure 2.3, each stick from the oxygen to the hydrogen atoms has a length of d_{OH} . The hydrogen atoms are separated from each other by an angle φ .

The values for these parameters (often accompanied by a few more)

Model	ρ (kg/m ³)	γ (10 ⁻² Pam)	μ (10 ⁻⁴ Pas)	D (10 ⁻⁹ m ² /s)	Cost
SPC	962	4.7	4.3	4.3	9
SPC/E	986	5.8	8.7	2.6	9
TIP3P	969	4.4	4.7	5.9	9
TIP4P	979	4.9	5.3	3.8	16
TIP5P	970	4.5	6.8	2.9	25
Experimental	996.5	7.17	8.54	2.3	-

TABLE 2.1 Properties of some popular water models at 300K and 1 bar. Measured by the author (experimental at 298K, from Krynicki, Green, and Sawyer 1978; Lemmon, McLinden, and Friend 2020). The computational cost increases with the square of the number of interaction sites.

make up a *water model*, a rough analogue to the more overreaching force fields previously introduced. A perfect water model would use values which make a collection of simulated water molecules behave as if they were real. A volume of such molecules would have the correct density ρ , viscosity μ , diffusivity D , surface tension γ and so on. These measures also change with the temperature T and pressure p , which a perfect model would have to capture.

As of writing this no perfect water model exists. All developed models are a trade-off between which values to capture well, in which conditions (like temperature and pressure) and how expensive they are from a computational view. A handful of popular water models are compared in table 2.1. For the work presented in this thesis we use the SPC/E water model (Berendsen, Grigera, and Straatsma 1987). This model captures several measurable properties well, while being computationally cheap. In addition, it is parametrised by fixing the dispersive C_6 term of the Lennard-Jones interaction (2.4) to its experimental value. Being a basic measure of internal molecular interactions, this is a good property to match against.

Water's crucial hydrogen bonding nature

Water may be a relatively simple molecule but one with a rich texture. Its properties are crucial for life as we know it. Its density as a solid (ice) is lower than as a liquid, which means that life can survive through the win-

ter at the bottom of lakes. It is a great solvent, which lets it carry salts and other crucial substances through nature. It even helps our bodies to assemble proteins and cell membranes at a rapid pace by acting as an accelerator.

These features stem from its ability to form *hydrogen bonds*. Hydrogen bonds—or, H-bonds—form between dipoles through the electrostatic interaction between a donor and an acceptor of two molecules. The donor atom “lends” an electronegative hydrogen atom site to the electropositive site of the acceptor. Due to the strength of Coulomb interaction the formed bond is quite strong, although not to the level of covalent bonds. They are transient but on aggregate form networks, which give water its high surface tension and viscosity.

Since hydrogen bonds are such a crucial part of water behaves they are an important feature to capture in simulations. Dipolar models, like SPC/E and the other models presented here, retain this ability. They are well suited for performing realistic computer experiments of liquids.

Simple liquids

Liquid molecules can be simplified by not considering electrostatic interactions. By only keeping the Lennard-Jones interaction between molecules simulations become cheaper to run and the software easier to write. The interactions are easy to tune by changing the involved interaction parameters to suit your needs. Moreover, many atoms can be strung together into chains to increase the viscosity.

However, such simple liquids will not retain the ability to form hydrogen bonds. Not only does this change the internal interactions of the liquid, as we will discuss later in this thesis it affects the mechanisms through which they move over surfaces.

To simulate a realistic system of water one has to include its dipolar nature. For this purpose simple Lennard-Jones liquids should be avoided.

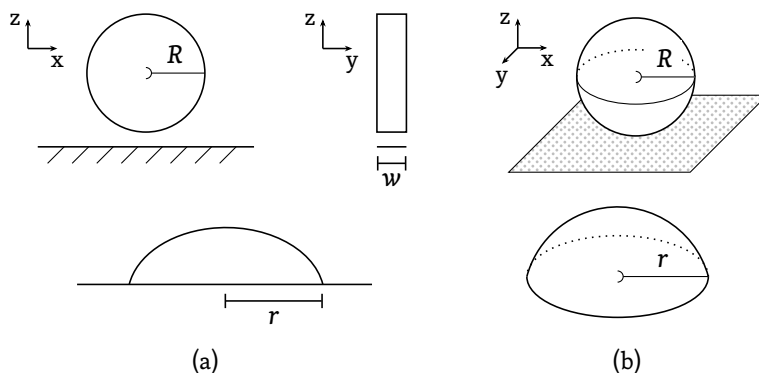


FIGURE 2.4 A water droplet of radius R constructed in two (a) and three (b) dimensions. For the two-dimensional case a periodic width w supplements the description.

2.3 Setting up a droplet computer experiment

A typical droplet experiment of spreading on a plate is conceptually very straightforward. First, a water droplet of some size is created some distance above the substrate. Second, the physics are initiated by adding thermal motion—temperature—to the system. This involves letting the system relax until it is stable. Finally, the droplet is gently brought into contact with the substrate, which initiates the spreading process.

This simplicity hides some subtle but important details. How large should the droplet be to represent a “realistic” system? Does the nature of the substrate have an effect, and if so how? Which boundary conditions are used? This section addresses a few of these questions.

Two- or three-dimensional systems

A real droplet experiment is usually performed with a spherical droplet. Unfortunately, spherical droplets are expensive to simulate using MD. A suitable alternative for some experiments may be to simulate a thin slice of the droplet. In this case the droplet is constructed as a cylinder instead of a sphere. It is replicated infinitely along the central axis using a periodic boundary condition. Figure 2.4 compares the two setups. Since the num-

ber of atoms increases by the radius squared in two dimensions versus the radius cubed in three, quasi-two dimensional systems are cheaper for the same initial radius.

Moving from three to two dimensions does not change any of the fundamental physics of wetting. It does however change the involved time scales of the spreading process. This is exemplified by Tanner's law, which predicts that $r(t) \sim t^n$ for the spreading radius r and experiment time t . The critical exponent n depends on which physics are dominating the spreading, but also varies depending on whether the system is two- or three-dimensional. Some scaling exponents with comparisons between two and three dimensions are collected in table II of Bonn et al. (2009).

Finite size effects and other computational artifacts

In a previous section we discussed the computational cost of simulating large systems using molecular dynamics. Still, thanks to concerted efforts to increase the efficiency of MD programs and the continued development of super computers, millions of atoms can now be simulated for tens or hundreds of nanoseconds.

While it is tempting to just use this power to construct larger and larger systems, we should ask ourselves why we need this in the first place. The most simple answer is that the system size directly affects two important aspects of a wetting experiment. For a small droplet, many molecules will lie at the surface. This means that surface energetics will dominate the wetting process. For larger droplets the surface-to-volume ratio decreases, meaning that inertia becomes a larger and possibly even dominating factor in the process.

There is also the possibility of finite size artifacts creeping in when systems are very small. For the case of water molecules, their interaction range with surrounding molecules is on the order of single nanometres. This sets a limit to how small the system can be to even have a bulk phase, or for a droplet cylinder how thin the system can be for molecules to not interact with themselves. A good rule of thumb is for the length scale of a system to be a few times the largest correlation length of components in

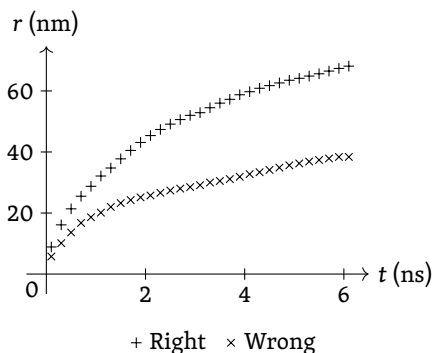


FIGURE 2.5 Spreading radius $r(t)$ for identical droplets with initial radius 50 nm, with correct and incorrect PME parameters. The incorrect parameters induce extra friction which slows the wetting.

the system to avoid these and similar artifacts.

Another artifact stemming from computer simulations relates to how long ranged non-bonded interactions are treated. As mentioned previously, it is common to only calculate Lennard-Jones interactions between atoms within a certain cutoff range, since the interaction decays very quickly. It has however been shown that this may introduce an artifact in for example anisotropic systems, where the dispersion term error adds up to be non-neglectable (Wennberg et al. 2013). This can be solved similarly to the Coulomb interaction, by using a PME summation of the potential on a grid in Fourier space.

For the systems presented in this thesis this has not been considered. However, a PME summation of the Coulomb interaction has been used to simulate correct long range electrostatics. When doing any PME computation it is important to consider the grid which charges are collected in the system. Charges are interpolated to the centre of the cell when performing the summation, which introduces an artifact if the grid is too coarse. Figure 2.5 shows how the spreading of a droplet can be affected by incorrect PME summation. Decreasing the Fourier cell spacing alleviates the issue.

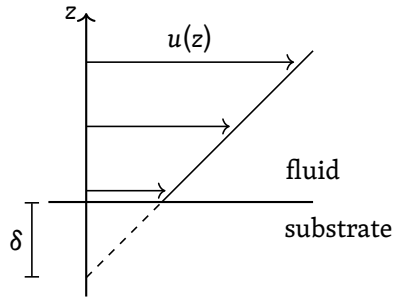


FIGURE 2.6 A liquid can slip along a substrate. The measure of slip is characterized by the slip length δ : an extrapolation of the flow profile $u(z)$ close to the interface.

Realistic substrates and hydrogen bonds

A large advantage of using molecular simulations is that we are not limited to reality when constructing experiments. This gives us the ability to hone in on specific effects, discarding phenomena which may hinder us from gaining knowledge in a real experiment. This freedom is double edged: it also means that we as system constructors have to ensure that all of the physics which are needed to model reality are present.

Wetting experiments contain at least two components, the liquid droplet and the substrate. So far we have discussed how to create a mostly realistic liquid. But what effects are needed to model a substrate?

In hydrodynamics, the substrate affects wetting in three terms. The first is through the system's thermodynamic properties: a substrate can either attract or repel a substrate to different degrees. If a liquid spreads out on a substrate, the substrate is classified as hydrophilic. If it contracts to a compact sphere, it is hydrophobic. This is determined by whether or not the system's free energy decreases or increases with a change in the liquid-substrate contact area.

Second, liquids can slip along some surfaces. How freely the liquid moves along a substrate is characterised by a *slip length* δ , shown in figure 2.6. A large slip length means that less energy is lost due to friction as the liquid spreads out on the surface—a hotly desired property for microfluidic systems which focus on fluid transport!

Finally, recent studies have shown that local effects at the triple contact line are an important source of energy dissipation for certain systems, in particular when the liquid cannot slip. This has been termed a *contact line friction*. It is as-yet unclear if and how substrate details affect this dissipation. It will be covered in more detail in chapter 3.

In molecular simulations these effects have to be included through the physics. The energetics are easily modelled by tuning the interaction parameters, for example the Lennard-Jones potential strength (the ϵ parameter) or the substrate charges. Fluid slip in turn arises due to a fluid molecule not forming a bond to a surface molecule, easily moving to adjacent sites. This is the case if for example only a Lennard-Jones interaction is present between the liquid and substrate molecules. Water molecules on the other hand form hydrogen bonds with other dipoles, which prohibit this motion.

In PAPER I we show that for substrates with identical surface tensions, the addition of hydrogen bonds alone results in zero liquid slip across the substrate. This results in different modes of contact line advancement, which we describe further in PAPER II. Hydrogen bonds have thus proven to be an important property for molecular wetting, which should be included when liquids like water is wetting certain substrates.

Spreading droplets on the nanoscale

CHAPTER THREE

While Young's equation (1.1) tells us how far a droplet will spread out on a plate, it says nothing about how it reaches that state. Understanding the process itself—the dynamics of wetting, or *dynamic wetting*—is important for any application which either moves droplets around or wants to optimise the process.

3.1 Models of dynamic wetting

Formal studies and theories of dynamic wetting began in the 1960s. Theoretical attempts to model the process roughly typically followed one of two approaches: looking at the contact line through the continuum view of fluid dynamics, or the molecular perspective of molecules jumping between adjacent potential minima sites of the substrate. Both approaches have had partial success as models, neither fully solving the problem. This suggests that different mechanisms dominate the process in different reg-

imes.

This section aims to provide a very brief overview of some modern theoretical models of wetting. Of most interest to this thesis is the *phase field method*, which blends molecular and continuum behaviour in an attractive package. Common to all is that the contact line is driven by a force F which is directly related to how far from equilibrium the droplet is. Following Young's equation (1.1) the non-equilibrium droplet state produces the driving force per length of contact line

$$\begin{aligned} F &= \gamma_{sv} - \gamma_{sl} - \gamma \cos \theta \\ &= \gamma \cos \theta_0 - \gamma \cos \theta \end{aligned} \tag{3.1}$$

for the involved surface tensions and current contact angle θ of the droplet.

In dynamic wetting it is preferred to not directly involve the equilibrium contact angle θ_0 in relations, but use the actual surface tension values. While θ_0 is a fantastic visual shorthand to the final state of a droplet, it is possible for $\gamma_{sv} - \gamma_{sl} > \gamma$, which cannot be represented using a modulating cosine. For the remainder of this chapter we will use the surface tension balance $S = (\gamma_{sv} - \gamma_{sl})/\gamma$ to represent the strength of wetting and refer to the equilibrium contact angle only when it is useful. The term S is often referred to as the *spreading coefficient* (de Gennes 1985).

Before moving on, we should first consider if Young's equation is valid at the molecular scales discussed in this thesis. Fortunately the answer is yes. Using MD simulations, Seveno, Blake, and De Coninck (2013) have shown that the predicted force F in (3.1) agrees with measurements down to the nanoscale. While a molecular contact angle may be more difficult to characterise, minimising the free energy of a system works at all scales.

Hydrodynamic model and the Huh-Scriven paradox

A popular approach to modelling wetting is by continuum theory. The Navier-Stokes equations model the flow of a system. The interfaces are treated by supplying appropriate boundary conditions, such as a slip length and the surface tension energy balance.

Knowing which boundary conditions to use and how has historically been a problem. Attempts made to model the contact line of a system with zero slip initially led to an infinite pressure at the (infinitely small) contact line, making any contact line advancement impossible. This is referred to as the *Huh-Scriven paradox* after its authors (Huh and Scriven 1971).

It is possible to regularise the singularity by changing the boundary condition. Further developments introduced, among other conditions, liquid slip across the substrate or pre-wetting films of some thickness. With more measurements over the past decades both effects have been observed for macroscopic droplet systems. A remaining limitation of the theory is that it depends on variables which have to be fitted instead of predicted from basic physics.

Molecular kinetic theory

Alongside the continuum theory development, the late sixties and early seventies saw another approach to modelling wetting. The work looked at advancement as a purely stochastic phenomena of molecules jumping between potential sites at the substrate. Using a purely molecular view gives the model its name: *molecular kinetic theory*, or MKT (Blake and Haynes 1969).

Equilibrium is reached when the advancing rate equals the receding, at which point the contact angle is at its static value. Reaching the equilibrium state is done at the predicted contact line velocity

$$v = 2\kappa\Lambda \sinh \{\beta F/2n\} \quad (3.2)$$

where κ is the rate at which molecules jump between lattices, Λ is the length of each jump and n is the number density of sites. $\beta = 1/k_{\text{B}}T$ is the inverse thermal energy for the Boltzmann constant k_{B} and temperature T , and F is the driving force (3.1) which introduces the dynamic dependency on the contact angle θ .

The model has been very successful at describing a wealth of experimental (Blake and Batts 2019; Blake and Shikhmurzaev 2002) and molec-

ular dynamics (De Coninck and Blake 2008) data from contact line experiments. Ren and E (2007) used an MD system to further develop an MKT-like boundary condition for contact line dissipation, which has been used to successfully model continuum simulations (Si Hadj Mohand et al. 2019).

A neat thing about the MKT model is that the mechanisms of contact line advancement is readily given through the variables κ , Λ and n , all of which relate more or less directly to the physical processes of the system. However, by measuring each variable in a molecular system system of water it has been found that (3.2) predicts a velocity an order of magnitude higher than that observed (as we report in PAPER 1). While the processes of a molecular system are more complicated than the simple origins listed for each variable, this still means that an accurate model of the contact line velocity—just like the continuum hydrodynamic models—hinges on using a fit to obtain the variables.

Phase field model

In the late nineties another approach came along. The phase field model looks at the system purely through its free energy, which it is trying to minimise by spreading out (Jacqmin 2000; Seppecher 1996). Here the contact line advances by the molecules diffusing over an interface of some width. Diffusion at the liquid interface obeys the Cahn–Hilliard equation (Cahn and Hilliard 1958).

An extension of the phase field model can allow for contact lines which do not have a constant contact angle θ_0 . This non-equilibrium boundary condition adds a dissipation term that is often referred to as a contact line friction, with units of viscosity (Carlson, Do-Quang, and Amberg 2011). While this term is not unique to diffuse interface methods (de Gennes 1985; Ren and E 2007) it appears here as a non-negotiable term if any deviation from θ_0 is to be seen.

A lot of attention has also been brought to the slip boundary condition used with phase field models. Phase field simulations have been used along with MD simulations to accurately match data using various types (Nakamura et al. 2013; Qian, X.-P. Wang, and Sheng 2003). We will return to

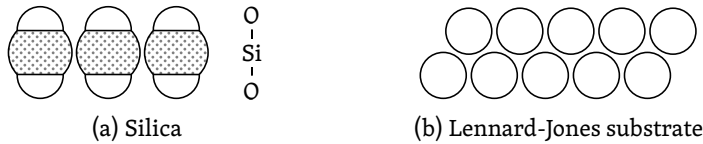


FIGURE 3.1 Side view of studied substrates. The silica consists of rigid SiO_2 molecules. Its atoms are charged, which induces hydrogen bonds with water molecules. The Lennard-Jones substrate atoms interact only using the Lennard-Jones potential.

these and the contact line friction condition in more detail throughout the remainder of this chapter.

3.2 Wetting on a molecular scale

By using molecular dynamics to study dynamic wetting we can investigate the process at a molecular scale. This approach gives us a lot of information for free. Since we can observe molecular events, we can observe how molecular processes affect the wetting. We can also measure properties such as slip lengths, jumping rates and other parameters. Since all models of wetting contain these or similar parameters, we can compare MD results to these models to infer if they are sufficient for a complete model.

Molecular substrate composition

As discussed in chapter 2, an advantage that MD simulations have over laboratory experiments is the ability to construct setups with specific characteristics. We use this to study the details of wetting in two cases: with a simple substrate built of atoms which interact only with a Lennard-Jones interaction (2.4), and a more complex—albeit idealised—silica substrate. This latter substrate’s complexity stems from being built out of rigid SiO_2 molecules. The rigidity is maintained by internal atomic bonds (2.3). The molecules are overall charge neutral but their atoms carry partial charges $q_{\text{Si}} = -2q_{\text{O}}$, making them electric quadrupoles.

The Coulomb interaction (2.6) between silica quadrupoles and water dipoles means that hydrogen bonds will form between the water and silica

Substrate	Tuning parameter			δ (nm)	$(\gamma_{sv} - \gamma_{sl})/\gamma$	θ_o ($^\circ$)
	Variable	Unit	Value			
Silica	q_o	e	-0.79	0.0	1.3	0
Silica	q_o	e	-0.74	0.0	0.81	36
Silica	q_o	e	-0.67	0.0	0.34	70
Lennard-Jones	ϵ	kJ/mol	1.77	1.1	0.80	37

TABLE 3.1 Properties of the studied substrates. Different energetics are achieved by tuning the listed parameter. Charges are given for the elementary charge e .

at close range. In turn, this removes the ability for water molecules to slip along the silica, setting the slip length δ to 0. Meanwhile, water cannot form hydrogen bonds with the Lennard-Jones substrate and will slip across it.

The composition of both substrates is shown in figure 3.1. Both are set in a tightly packed face centred cubic formation, although the silica consists of a single layer only. An overview of the substrate properties and how the interaction strengths are tuned to achieve different surface energetics is given in table 3.1.

Profile of the driving force

How quickly the contact line advances will depend on the strength of the driving force F (3.1). It is interesting to consider exactly how this force is applied to the liquid molecules. Since MD simulations lets us access molecular forces this can be investigated for our substrates, which allows us to compare how the two different substrates interact with our water droplets.

The measurement is done by restraining a slab of water to a height h above the substrate and noting the force with which the substrate is pulling on it. Repeating the measurement for many different heights produces a force profile[†]. In PAPER I we measure the force for the introduced silica

[†]Integrating this force profile (PMF) yields exactly $\gamma_{sv} - \gamma_{sl}$ —a very efficient method for measuring the system energetics.

and Lennard-Jones substrates and see that it is very short ranged. Indeed, it has a range of less than 0.3 nm from the substrate atoms which is barely enough to cover the first layer of water molecules.

In effect, this means that even if the force F can be very strong it is only acting on a very small part of the liquid. If the bottom layer of the liquid is immobilised—as it is on no-slip substrates like our hydrogen bonding silica—there are few mobile molecules which the driving force can act on. As we will discuss in the next section this has large consequences for contact line advancement.

Matching molecular simulations to continuum models

MD simulations give us access to an experimental method for studying wetting phenomena. Just as for laboratory experiments we can use them to evaluate theoretical models.

One has to take some care when making these comparisons. Continuum methods model wetting systems through different parameters, such as viscosity μ , surface tension γ , slip length δ and so on. As discussed in chapter 2 these can be measured in MD simulations. A proper simulation procedure for these comparisons is to measure as many properties as possible, to limit the number of free parameters which need to be used. Any observed discrepancies may highlight in which ways the studied models cannot describe reality.

In PAPER III we apply this approach to a shear flow system. A water slab is entrenched between two plates of no-slip silica which move in opposite directions to create a shear. This system is ideal for a simple comparison of models, since it involves a steady state with multiple moving contact lines (one receding and one advancing per surface). Simulations can be extended indefinitely to gather more data, which is only possible in droplet experiments by repeating them. Using our MD setup to measure all free parameters we use numerical phase field and volume of fluid simulations to evaluate continuum models.

What we find is that both methods accurately capture the global dynamics of the system. However, close to the contact line we see that the

details diverge. The phase field method in particular displays a continuous and large flow across the interface, which is not observed in the MD experiment. Instead, by relaxing our constraint of only using MD measured parameters we obtain a better match by increasing the diffusion term in phase field far beyond what is seen.

The difference between the continuum slip boundary conditions are also investigated. The regular Navier slip boundary condition is compared to the generalised Navier boundary condition (Qian, X.-P. Wang, and Sheng 2003). Notably, both encounter the same issue with regards to the velocity field at the contact line in the phase field model not matching that of the MD simulations.

While this shows that both phase field and volume of fluid methods can replicate an MD experiment it is unsatisfactory to require a free fitting parameter. It suggests that there is some fundamental process from molecular wetting that the models are not capturing. Further investigation into these effects is needed to resolve this discrepancy.

3.3 Contact line friction

As discussed earlier, theoretical models of wetting have predicted that there may be a source of dissipation locally at the contact line (Carlson, Do-Quang, and Amberg 2011; de Gennes 1985). Due to how contact line area is fixed in size to a few nanometres, these effects have not been important to model correctly for large droplets. Until recently few formal studies of the nature of the dissipation have been published.

For water droplet nanoscale systems the contact line area is no longer insignificant. Sensitive force measurements have shown an extra source of friction attributed to this local source. It has been attributed to nanoscale defects that the contact line pins to (Perrin et al. 2016) as well as slip dissipation (Nakamura et al. 2013), but also seen for systems discussed in this thesis: defect-free substrates with zero slip. This motivates our study of the molecular source of dissipation, which is related to the details of how the contact line advances.

Substrate	$(\gamma_{sv} - \gamma_{sl})/\gamma$	\dot{E}_f/\dot{E}_γ	$\hat{\mu}_f (\mu)$
Silica	1.3	0.7	5.3
Silica	0.81	0.5	4.3
Silica	0.34	0.4	3.3
Lennard-Jones	0.80	0.2	-

TABLE 3.2 Contact line dissipation rates \dot{E}_f compared to the rate \dot{E}_γ at which energy is fed into the system as droplets spread on different substrates. Measured contact line friction parameters $\hat{\mu}_f$ are listed alongside.

Contact line friction in molecular systems

As the wetting moves from an inertially dominated stage to one dominated by viscous friction, the dynamics slow down considerably. A driving force is necessary to keep the contact line moving against all the viscous friction. In such a state, the contact line velocity v has been shown to be proportional to this driving force F (Yue and Feng 2011):

$$v = \frac{F}{\mu_f} = \frac{\gamma_{sv} - \gamma_{sl} - \gamma \cos \theta}{\mu_f}. \quad (3.3)$$

The dissipation is contained in the μ_f factor, which has units of viscosity.

Note that we can measure both the contact line velocity and contact angle. This leaves (3.3) with the dissipation as its single unknown variable. Furthermore, the rate of dissipation \dot{E}_f can be calculated by

$$\dot{E}_f \approx l\mu_f v^2 \quad (3.4)$$

for the total length of the contact line l (Carlson, Bellani, and Amberg 2012; de Gennes 1985; de Ruijter, De Coninck, and Oshanin 1999). Taken together this means that an easy measurement of the dissipation term is possible, which then allows us to measure the total rate of dissipation from the contact line.

Doing so for our molecular systems with and without slip (respectively a Lennard-Jones substrate and a silica-like) reveals two things. One is that the contact line dissipation is lower if the liquid can slip across the substrate than when it cannot. This is shown in table 3.2 by comparing the

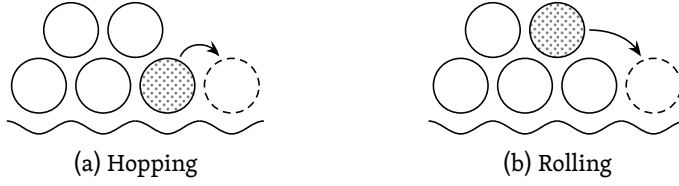


FIGURE 3.2 Molecular modes of contact line advancement. The substrate is drawn as a potential landscape.

dissipation rate to the rate at which energy is gained from the liquid covering a larger area \dot{E}_Y , which is measured by

$$\dot{E}_Y = [lv(\gamma_{sv} - \gamma_{sl}) - \gamma\Omega] \quad (3.5)$$

where Ω is the rate at which the liquid-vapour interface area changes.

The second is that the dissipation factor μ_f is largely constant if the liquid can slip across the substrate, but increases during the experiments if it cannot. This suggests that the dissipation is dependent on the details of how the contact line advances. From now on we will focus on the case of no-slip substrates and investigate how the advancement can lead to this dissipation.

How the contact line advances in the case of no slip

If we consider how a droplet contact line can advance in a no-slip scenario, we can propose two separate possibilities: the current wetting edge moving outwards, or new fluid molecules filling in from above to construct a new edge. In the former case the outermost molecule hops from one potential minima to an empty adjacent minima. In the latter a molecule at the interface rolls over the edge in to a minima. Figure 3.2 shows these modes.

The two modes work with slightly different mechanisms. For the hopping mode, the potential barrier for an advancing event is set by the substrate interaction. For example, in the case of a hydrogen bonding liquid and substrate, the molecule has to break this relatively strong bond in order to move forwards before it can form a new hydrogen bond with the

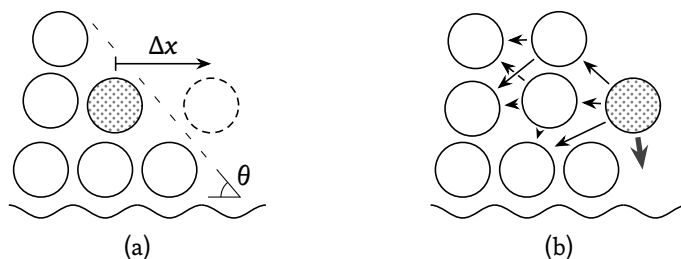


FIGURE 3.3 Surrounding molecules create a potential energy barrier for reaching the edge and dropping down. The energy barrier depends on the contact line wedge geometry.

substrate. Meanwhile, the rolling mode is not hindered by breaking a hydrogen bond with the substrate, but by its surrounding liquid molecules that want to keep it close.

Since molecular simulations give us the particle trajectories, we can measure how prevalent these modes are in dynamic wetting. In PAPER II we do so and see that for a no-slip silica substrate, both modes contribute to a substantial part of the advancement. In the inertial regime, the rolling mode is more common, while in the viscous regime the hopping mode is roughly two thirds of all advancing events.

One should note that these modes are simplifications of what happens at a molecular contact line. The contact line does not advance through single, clearly defined events. Rather, the advancement occurs in a connected network of liquid molecules. As a molecule hops to fill one space, another should quickly move in to occupy its previous place. How these interconnected motions affect the wetting modes is not yet understood.

Energy barrier for rolling mode

This gives the rolling mode a subtle dependency on the geometry of the wetting edge. If the wetting is not dominated by an inertial flow, a boundary molecule has to cross the barrier by a thermal fluctuation. The fluctuation has to be large enough for the molecule to pass over the edge, after which it can drop onto the substrate.

From geometry, sketched in figure 3.3, we infer that a lower contact

angle θ means that the thermal fluctuation has to be larger, as the molecule has to cross a larger distance Δx . In molecular diameters this distance will on average be $\Delta x = \tan(90^\circ - \theta) + d$, where d is how far past the edge the molecule has to be before dropping down. A thermal fluctuation which covers this distance has to be of size $h = \Delta x \sin \theta$, since the fluctuation is perpendicular to the liquid interface. Expanding Δx and using some trigonometric identities we see that

$$\begin{aligned} h &= \sin \theta [\tan(90^\circ - \theta) + d] \\ &= \cos \theta + d \sin \theta. \end{aligned} \tag{3.6}$$

In order to create a fluctuation the system uses energy ΔE proportional to the created surface area, which means that $\Delta E \sim h^2$. This is the average potential energy barrier for a rolling event to occur. Following Maxwell-Boltzmann statistics we know that the probability P for such an event is given by the exponential

$$\begin{aligned} P &\sim \exp\{-\beta \Delta E\} \\ &= \exp\{-a\beta (\cos \theta + d \sin \theta)^2\} \end{aligned} \tag{3.7}$$

where a is an unknown energy scale and $\beta = 1/k_B T$ again the inverse thermal energy of the contact line.

This equation contains a few noteworthy features. The barrier tends towards zero as the contact angle θ increases, up to and including the point where $\cos \theta = -d \sin \theta$. This behaviour represents that it's easy for liquid molecules to roll down onto the substrate when they do not have to pass the contact line edge—they simply have to come within the substrate interaction range. Note that the equation is invalid for θ larger than the last criteria, since the rolling molecule at that point does not have to cross the edge as used in the model[†].

For contact angles decreasing from 90° the energy barrier rapidly in-

[†]To be precise, equation (3.7) is well defined for the interval $0^\circ < \theta \leq 180^\circ - \operatorname{arccot} d$. The overhang factor d cannot be precisely measured. We here take it as 0.5: one-half of the molecule diameter.

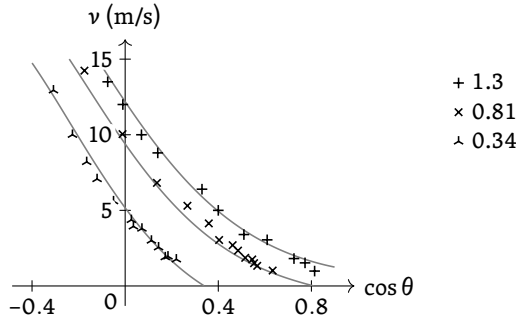


FIGURE 3.4 Velocity and contact angle data from droplet system simulations with different values of the spreading coefficient $S = (\gamma_{sv} - \gamma_{sl})/\gamma$. Each set is overlaid onto the prediction of equation (3.8). Originally published in PAPER II, recreated with permission.

creases at first but levels off as it approaches 0° . The rolling mode becomes less probable to be observed for small contact angles. This is consistent with observations.

Model for molecular contact line friction

With a very simplified argument we have introduced the probability of the contact line advancing through a liquid molecule rolling onto the substrate from an upper layer. Since molecules want to stay together and cannot be easily pulled to the substrate by the driving force F , the advancement is slowed down compared to if they were free to drop down. This energy barrier is the reason for why measured contact line velocities v are lower than expected from older continuum models.

This slowdown can be implemented into continuum models. The rate of advancing events is proportional to the probability P of advancement (3.7). In effect, this means that we modulate the velocity that would be expected from a given driving force by this probability (3.3), yielding

$$v = \frac{F}{\hat{\mu}_f} \exp \{-a\beta (\cos \theta + d \sin \theta)^2\}. \quad (3.8)$$

Here $\hat{\mu}_f$ is a contact line friction factor which has units of viscosity and

depends on the used system. Since the energy scale a represents the potential energy barrier it depends on the used liquid, leaving $\hat{\mu}_f$ as a single free parameter which can be measured for systems. For the water-on-silica systems presented in this thesis, the value $a = 1.1k_B T$ along with the given values for $\hat{\mu}_f$ in table 3.2 produce excellent agreement with the simulation data. Figure 3.4 displays this comparison. Our proposed model thus successfully captures contact line friction in these experiments.

In addition, the model can explain how the energy from the contact line slowing down is lost. To reach the crossing state shown in figure 3.3b a molecule has temporarily borrowed thermal energy from its neighbours. Once it falls onto the substrate and forms a hydrogen bond this energy is converted into kinetic energy, which is then dissipated into its new environment. While the exact details of how this energy is dissipated—for example, how much is lost by dissipation into the substrate or returned to the liquid as it extends over it—are unknown, this model provides a molecular mechanism and an interesting avenue for future exploration.

Molecular electrowetting

CHAPTER FOUR

A droplet will spontaneously spread out when placed on a plate to an extent determined by the involved surface energetics. For a long time there has existed a desire to manipulate these energetics to achieve a specific effect. Researchers have for example created heterogeneous surfaces with stripes of varying wettability and micro-structures to decrease or increase the effective friction.

Such surfaces are still static. To freely change the properties of a system, for example to move a liquid around or spread out and retract on command, another approach is needed. So far the most popular candidate has been applying an electric potential to the liquid, a technique known as *electrowetting* which was experimentally shown and modelled by Gabriel Lippmann (1875).

Active surfaces have a wide range of applications in areas such as dynamic camera lenses, controlled microfluidic transport and display technology. Understanding the physics and processes of electrowetting thus

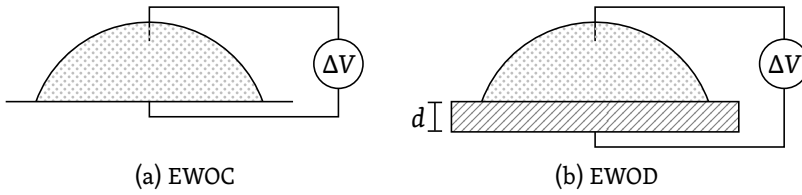


FIGURE 4.1 Electrowetting setups in the two widely used configurations: on a conductor (a) and a dielectric film of thickness d and permittivity ϵ_d (b).

may be a great step forward for microfluidic research in the 21st century.

4.1 Physics of electrowetting

In a very simplified configuration an electrowetting system consists of a liquid droplet—typically an electrolyte solution—placed on a conducting substrate, with a potentiostat coupled between the substrate and an inserted electrode as sketched in figure 4.1a. Using the potentiostat an electrostatic potential ΔV is applied. The droplet spreads out in response to this field as ions are accelerated along it, trying to minimise their energy.

In effect, this changes the surface tension γ_{SL} between the droplet and the conducting substrate as

$$\gamma_{SL}^* = \gamma_{SL} - \frac{C \Delta V^2}{2} \quad (4.1)$$

where C is the capacitance of the conductor. Since we know that the surface tension is directly related to the static contact angle θ_0 through Young's equation (1.1) we can predict how the spreading changes by calculating how much the surface tension changes. This results in a modified version known as the *Young-Lippmann equation*:

$$\begin{aligned} \gamma \cos \theta_0^* &= \gamma_{SV} - \gamma_{SL}^* \\ &= \gamma_{SV} - \gamma_{SL} + \frac{C \Delta V^2}{2}. \end{aligned} \quad (4.2)$$

This equation is the basic model used in all of electrowetting.

Wetting on conductors versus dielectrics

While equation (4.2) describes the energetics of electrowetting systems there are some practical complications when wetting on pure conducting surfaces. The direct contact between the ions and conductor results in electrolysis, a chemical reaction wherein ions are permanently[†] absorbed by the substrate. This means that the wetting is not reversible, which is desired for most all systems—a camera lens has to predictably spread out and retract every time the potential is changed.

A solution to this problem is to insert a thin, insulating, dielectric film between the conductor and droplet, shown in figure 4.1b (Berge 1993). This film will decrease or eliminate the absorption and can be constructed with some desired properties, like hydrophobicity and low friction. The downside is that the film's thickness d lowers the strength of the electric field which means that a larger applied potential ΔV is required for the same change in contact angle θ_o^* . For such a system equation (4.2) can be rewritten as (Mugele and Baret 2005; Zhao and Y. Wang 2013)

$$\gamma \cos \theta_o^* = \gamma_{sv} - \gamma_{sl} + \frac{\epsilon_o \epsilon_d \Delta V^2}{2d} \quad (4.3)$$

where ϵ_o and ϵ_d respectively are the electric permittivities of vacuum and the dielectric. Compared to electrowetting on conductor (EWOC) setups which require on the order of single Volts to affect a large change in contact angle, these electrowetting on dielectric (EWOD) setups may require several hundred Volts for similar changes.

More recently the interest in EWOC configurations has been reignited due to the advent of cheap and accessible graphene substrates. Graphene is an excellent conductor and chemically stable, with little to no absorption of ions. It has been shown to provide reversible wetting with large contact angle changes for very low voltages (Lomax et al. 2016). For this thesis, similar EWOC systems to these are used.

[†]At least as considered for practical applications, where processes can repeat hundreds of times every second.

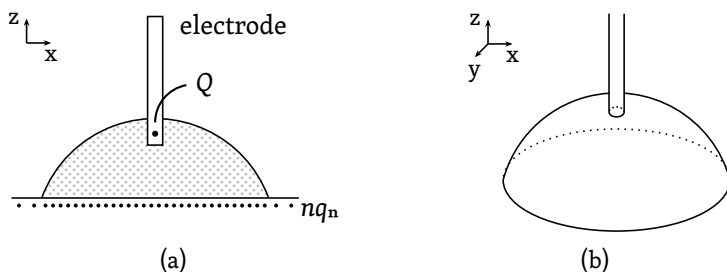


FIGURE 4.2 Molecular dynamics setup for electrowetting. A two-dimensional cross section shows the components (a). The electric field is created by n charges of strength q_n which can move freely below the substrate and a single charge Q in the electrode. The inserted electrode means that simulations must be three-dimensional (b).

4.2 Reconstructing an electrowetting setup

A realistic depiction of an EWOC system requires that all the components described above are modelled: a conducting substrate, an electrode and a liquid droplet. We have previously described how to create molecular substrates, but it has to be restated that most molecular dynamics methods are purely classical. This means that we cannot accurately or cheaply mimic the physics of an electric conductor, which requires us to treat free electrons.

However, for the purpose of simulating electrowetting we only need an electric field between the substrate and the electrode. Accurately modelling how a conductor creates this field is beyond the scope of this thesis—we simply create the field by adding a monolayer of n charges q_n below the substrate. These charges are free to move in the transverse plane of wetting but fixed in the normal direction.

Similarly, the electrode is created as a thin carbon nanotube which is closed in both ends. A single charge $Q = -nq_n$ is fixed near the bottom of this electrode, setting it to exactly neutralise the “conductor” charge while directing the field into the electrode. By tuning the total charge we tune the strength of the electric field and thus the applied electric potential ΔV . This setup is shown in figure 4.2.

In chapter 2 we discussed the difference between two- and three-dimensional systems. For spontaneous wetting on homogeneous substrates this difference comes down to a scaling factor which means that two-dimensional simulations will describe the physics of a three-dimensional system after this is taken into account. Note that the addition of an electrode removes this option. An infinitely replicated (through the periodic boundary condition) electrode is a perpendicular substrate, not anything resembling a tube. In order to simulate a conductor–droplet–electrode setup, we have to use fully three-dimensional systems.

Electrolyte solutions are created by adding ions to a pure water (SPC/E) base to the desired concentration. Force field parameters for these ions have been previously reported (Hess and van der Vegt 2009; Weerasinghe and Smith 2003).

4.3 Reduction of contact line friction

Curiously, it has been shown that contact line friction—as discussed in chapter 3—is consistently absent under electrowetting conditions. Even for micro-structured systems which create a lot of friction during spontaneous wetting the dissipation mostly vanishes when an electric field is applied (Decamps and De Coninck 2000; Nita et al. 2018). Since the friction of these system arises from microsized structures on the substrate, this effect has been referred to as *cloaking* the surface features.

By simulating molecular electrowetting on the previously introduced high-friction silica substrates we show in PAPER IV that this effect remains on a molecular level. The line friction decreases by an order of magnitude and the spreading changes from being dominated by it to inertia being the dominant factor inhibiting the process. It is thus not only a cloaking of surface features, since these surfaces have none, but of line friction on a molecular basis.

Electrostatic bias of the advancement energy barrier

Just as when seeing that no-slip substrates show a lot of line friction, we return here to the question of what physical phenomena is causing this massive decrease in it. We previously (in chapter 3) introduced a model of the line friction arising from an energy barrier that has to be crossed by a liquid molecule to advance the contact line. Since the substrate-to-liquid interaction has an extremely short range water molecules are not assisted in crossing this barrier.

In an electrowetting system this situation changes. The potential difference ΔV between the electrode and conducting substrate creates an electric field \vec{E} throughout the system. Any charge q in the system experiences a force

$$\vec{F} = q\vec{E} \quad (4.4)$$

from this field. Not only that, overall charge neutral but polar molecules will experience a force

$$\vec{F} = (\vec{p} \cdot \nabla)\vec{E}, \quad (4.5)$$

where \vec{p} is the polar moment of the molecule. This latter force comes from how the forces (4.4) working on individual charges in a molecule do not cancel if the electric field changes over it.

At the moving contact line an electric field and both of these forces are present. By measuring the electric field and polar moments of water at the contact line, we show in PAPER IV that the force of equation (4.5) in electrowetting is both significant and long ranged. An *electrostatic bias* is added, diminishing the energy barrier of equation (3.8). Contact line friction is removed and the contact line can advance at the rapid pace seen in experiments.

The importance of realistic systems

Contact line friction being diminished in electrowetting stems from several features of water. It is an electric dipole, which allows it to form hydrogen bonds. Hydrogen bonding to substrates occurs naturally and results in a molecular no-slip condition. If a contact line cannot slip it has

to advance by non-bonded water molecules rolling in from above, which requires crossing an energy barrier. Finally, this barrier is diminished in electrowetting by the electric field working to pull the dipoles across it.

If this long chain of consequences starts with water being a dipole we again see how important this feature is. As we discussed in chapter 2 this is a feature which simple Lennard-Jones liquids lack. While such liquids simplify computations they fundamentally cannot be used as a substitute if realistic effects are studied.

To study reality we need to describe it.

Outlook

CHAPTER FIVE

The field of wetting has been studied for several hundreds of years but still poses interesting and challenging questions for modern researchers. As we are now probing systems in the mesoscopic regime where nanoscale or even molecular effects enter into play I can only see these questions remaining important over the foreseeable future.

To be more specific we still lack a holistic view of how a contact line moves or retracts. It is easy to imagine simple models such as how it pins to defects, but when the thermal motions of molecule groups are important these motions become more complicated. The model that has been presented on contact line motion and how line friction is related to an energy barrier that has to be crossed through thermal activation is still very simplified compared to the chaotic events at an actual triple point, but it is a clear example of how these events may be characterised to better understand molecular wetting.

With how complex and chaotic these events appear one may ask the

question of whether understanding them is a requirement if one can just simulate any system in a computer. After all, the state of molecular dynamics simulations and supercomputing has advanced to the point where systems spanning tens to hundreds of nanometres in either direction can be simulated over tens to hundreds of nanoseconds given sufficient (large but realistic) resources. Moreover, their use has been accepted in several fields as a valid complement to or even pioneering of real world experiments and phenomena. For these accomplishments of molecular dynamics, Martin Karplus, Michael Levitt and Arieh Warsheh were awarded the 2013 Nobel prize in chemistry.

The question is valid, if somewhat misguided since fundamental knowledge is of its own value. Certainly in the near future one can imagine constructing suitably detailed systems emulating an industrial process and throwing a large computer at it. Techniques such as coarse-graining the simulation can be used to further reduce the limitations of scaling while keeping essential physics.

It should be kept in mind though that something being possible does not make it a clever use of resources. As molecular effects largely manifest at interfaces they are not crucial to model in a large part of a droplet experiment. Incorporating them through a boundary condition for a continuum simulation may be a faster and smarter way to the same result (Carlson, Do-Quang, and Amberg 2011; Qian, X.-P. Wang, and Sheng 2003; Ren and E 2007; Zhang, Borg, and Reese 2017). Similarly, simulating a millimeter length channel or flow through an array of shorter channels may not need a full atomistic treatment as the flow will be similar throughout the repetitions. Here molecular dynamics can be used to simulate selected parts of the system, like the channel openings or one selected channel, and a continuum model can be coupled to that simulation to evolve the remainder (Borg, Lockerby, and Reese 2013).

These treatments fall under the domain of *multi scale modelling*. While not a new field in any sense of the word, there are no—and possibly should not be any due to different systems having different physics—unified ways to incorporate molecular and continuum effects for different types of sys-

tems. Furthering the development of these techniques will be an important part of modelling mesoscopic fluid systems in the 21st century.

In this sense, molecular simulations of liquids are and will continue to be a powerful tool to understand and model processes in wetting. For small scale systems by these methods making few assumptions of the needed physics and for large scale systems by including these effects in an indirect way.

The work presented in this thesis has shown that even simple molecular processes can propagate to large scale wetting. In contact line dynamics by having to cross a energy barrier which is molecular in nature. In electrowetting by being assisted over this barrier. It is clear that molecular effects are important to study to better describe wetting processes. Whether we incorporate these effects by fully molecular simulations, multi scale modelling or better boundary conditions for continuum models is an open question, but they simply cannot be ignored.

Summary of papers

From the very inclusive term “molecular processes” in the title of this thesis, the work has mostly centred around understanding how these processes contribute to contact line advancement in dynamic wetting. Papers I, II and IV attempt to describe these dynamics in different contexts. PAPER III follows in the footsteps of PAPER I by comparing our MD simulations to continuum models of wetting in a detailed shear flow setup.

Paper I: Water–substrate physico-chemistry in wetting dynamics

This is the first attempt to understand how substrate features play into contact line friction. Three MD systems with water and widely different substrates are created: one consisting of a purely repelling force wall, which has no features whatsoever, one being an atomistic Lennard-Jones substrate and one being a silica-like substrate consisting of electrostatic quadrupoles.

The substrates have identical surface tensions and equilibrate to the same static contact angle θ_0 . The systems are characterised by measuring all the variables that are required for continuum models, with the only change between them being the slip length. The pure force wall has infinite slip length (free slip), the Lennard-Jones substrate a slip length of 1.1 nm and the silica-like no slip at all.

Spontaneous wetting experiments are performed for these systems and compared to continuum phase-field simulations which use the measured variables including the slip length, instead of involving these as free parameters for a fit. We find that even when accounting for the slip length, the systems cannot be described with a single contact line friction parameter. This shows that contact line friction is a complex process involving the details of how a liquid moves along the substrates. The range of the driving force acting on the water from the substrates is measured and for the most realistic setup found to be on the range of the first layer of water molecules. We conclude that energetic properties are not sufficient to fully characterise the wetting of a system.

Paper II: Molecular origin of contact line friction in dynamic wetting

Continuing the work begun in PAPER I this paper characterises the contact line friction seen on the no-slip silica substrate. The substrate energies are varied to give contact angles θ_0 from 0° to 70° . MD simulations of spontaneous wetting is performed and the contact line friction measured during the process.

We see that the contact line friction is not only a large source of energy dissipation, it varies both with the substrate energetics and during the simulations themselves. In particular, as the droplets spread out the friction increases. We furthermore observe whether the contact line advances by MKT-like jumps or by molecules rolling in from upper water layers and find that both modes are present in the later stages of wetting.

A model is presented which relates the changing friction to the geom-

etry at the contact line. As the contact line evolves the geometry results in a higher energy barrier that molecules have to pass in a thermal fluctuation to advance the line. This energy is lost after passing the barrier, as the energy is dissipated into the surroundings. The model is shown to agree well with the measured friction as it evolves during all simulations.

Paper III: Steady moving contact line of water over a no-slip substrate

Molecular dynamics simulations of a shear flow of water through a channel are used as a basis of comparison for phase field and volume of fluid simulations. Different boundary conditions for the numerical models are triaged with parameters measured from the MD simulations.

It is established that neither the phase field nor volume of fluid methods can replicate the MD experiment. While the global system density profile is easily matched for both, the details local to the contact line are not consistent with the molecular motions in MD. By tuning various parameters away from those measured in MD a better agreement is found. However, this is by itself inconsistent with the MD data which suggests that some processes around the contact line are not described by the numerical models.

Paper IV: Electrowetting diminishes contact line friction in molecular wetting

The contact line friction condition is investigated in the context of electrowetting. Molecular dynamics systems are created with pure water and a KCl electrolyte solution wetting on a no-slip silica substrate. The electric field is applied and contact line friction measured as the droplets spread out to their final contact angles θ_0^* .

We find that the electrowetting condition reduces the contact line friction by an order of magnitude. A system which was previously dominated by the line friction dissipation in spontaneous wetting is instead domi-

nated by inertial acceleration as the electric field is applied. This is discussed in the context of the previously suggested model of contact line friction. We propose that the reduction in contact line friction may be due to the electric field reducing the energy barrier that molecules have to pass to advance the line.

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