Dynamic wetting: status and prospective of single particle based experiments and simulations
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Abstract

The fundamental molecular and microscopic properties of materials leading to dynamic wetting and relaxation effects have been subject to numerous studies in the past decades, but a thorough understanding is still missing. While most previous experiments utilize fluids deposited on planar substrates, this article focuses on an attractive alternative based on single colloidal particles: colloidal particles have the ability to strongly interact with fluid-fluid interfaces and the behavior strongly depends on the surface properties of the particles and the fluids used. Recent progress in the manipulation and synthesis of colloidal particles with well-defined surface properties and shapes makes them ideal candidates to probe the fundamental surface properties leading to dynamic wetting effects. In this paper we review and discuss the status of experimental and numerical techniques to characterize the dynamic wetting of single particles at fluid-fluid interfaces, with the aim to assist scientists and engineers in the design of new experimental techniques and particle-based (bio)analytical tools.

KEYWORDS: colloid; fluid interface; contact angle; dynamic wetting; contact angle relaxation; magnetic tweezers
In the early 20th century the pioneering work of Ramsden and Pickering [1,2] demonstrated that colloidal particles can be used to stabilize emulsions by adsorption at liquid interfaces. In 1980 Pieranski [3] described the adsorption energy in terms of the surface tension of the fluid-fluid interface and the particle wettability by the fluids, showing that for micrometer-sized particles the depth of the potential well is several orders of magnitude greater than the thermal energy. The strong adsorption of colloidal particles at fluid interfaces is being used in a wide range of applications. In froth flotation for example, the adsorption of particles is exploited for mineral extraction [4]. More recently particle assembly at fluid interfaces has been studied as a platform for the design of novel colloid-based materials [5–13]. In addition, the interaction between particles and fluid interfaces is important for the field of lab-on-a-chip biosensing, where particles are used for their large surface-to-volume ratio, flexible bio-functionalization, stability, and for their actuation and detection properties (see e.g. [14]).

Wetting on planar surfaces has already been studied in 1805 when Young described the interaction of fluids with planar substrates [15]. The surface wetting is characterized by the interfacial tensions and the resulting equilibrium contact angle, see Fig. 1a. The static contact angle refers to the equilibrium state. The contact angle changes in an out-of-equilibrium situation and is often described by a dynamic contact angle that has a directional and time-dependent character, with values for advancing and receding states, contact angle hysteresis, and contact angle relaxation, see Fig. 1b. Wetting happens at different temporal and spatial scales, but mostly only macroscopic observables, such as viscosity, surface tension, wetting speed and dynamic contact angle, are accessible. Static and dynamic wetting have been the center of many studies over decades and there are several experimental techniques available. Nonetheless, the micro- and molecular-scale origin of wetting phenomena complicates the development of model descriptions and leaves still many questions unanswered about the underlying physical mechanisms of contact line motion [16–22].

Colloidal particles at fluid-fluid interfaces are characterized by the three-phase contact angle formed between the two fluids and the solid particle [5], see Fig. 1c. The small size of the particles (from a few nanometers to several micrometers) and the optical discontinuity between the two fluid phases makes the direct measurement of the contact angle challenging. Several approaches have been reported in literature to measure static contact angles on particles, in the form of an ensemble measurement that records an average contact angle over many particles [23–28] or a measurement that yields the contact angle of individual particles [29–37]. These techniques measure a static value for the contact angle and neglect dynamic effects.

Recently it has been shown that the relaxation process of particles adsorbing into fluid-fluid interfaces can have a very long tail with contact line speeds as low as $10^{-1} \mu m/s$ [38–40]. A description based on capillary forces and hydrodynamic friction predicts initial speeds in the order of a few $m/s$ and relaxation times in the order of $\mu s$ [38,41]. These observations call for the development of methods to quantify and model dynamic wetting effects on colloids over a broad range of time and energy scales, preferably at the level of individual particles and suitable for a wide range of particle types, surface functionalizations, and fluid properties.

While a vast literature on numerical simulations of problems involving wetting is available, we limit ourselves to review contributions which utilize microscale algorithms such as molecular dynamics or mesoscale algorithms such as the lattice Boltzmann method. Molecular dynamics simulations describe a system in terms of individual particles following Newton’s equations of motion. Interactions between
these particles ("molecules") are commonly implemented in terms of parameterized Lennard-Jones potentials to define the interaction of fluid and surface species. Due to the prohibitive computational cost of molecular dynamics simulations, they are generally limited to temporal and spatial ranges on the nanoscale. The lattice Boltzmann method overcomes this problem at the price of eliminating the molecular details of the involved materials. It is based on a phase space discretization of Boltzmann’s equation, several multiphase extensions exist and the implementation of complex geometries is exceptionally easy. Combined with the molecular dynamics algorithm, it is used to simulate particles with arbitrary shape, adjustable wettability, or different particle-particle interactions suspended in fluid. The method has become a mature alternative to classical computational fluid dynamics methods and is very popular in applications reviewed in this paper.

In this paper we review and discuss the status of experimental and numerical techniques to characterize the dynamic wetting of single particles at fluid-fluid interfaces, following the scheme presented in Fig. 1. First we introduce the basic notions of wetting on planar substrates through Young’s equation and the related techniques to measure static and dynamic contact angles (Fig. 1a, b) and we focus on the unanswered questions about the origin and scaling relationships of dynamic wetting. Thereafter we outline experimental and numerical techniques to study static (Fig 1c) and dynamic (Fig. 1d) wetting on single particles at fluid-fluid interfaces. Finally we conclude by discussing the status and future of single particle based experimental techniques, which in combination with numerical tools should help scientists and engineers to tackle a wide range of challenges that require to be predictive and to have exquisite control on the wetting behavior at different spatial and temporal scales. We expect that the resulting understanding and materials control should lead to novel bottom-up approaches in the field of colloidal self-assembly and novel particle-based concepts for miniaturized (bio)analytical tools.

**CONTACT ANGLE ON PLANAR SUBSTRATES**

*Static contact angle*

"For each combination of a solid and a fluid, there is an appropriate angle of contact between the surfaces of the fluid, exposed to the air, and to the solid" [15]. Two hundred years later, the measurement of contact angles is still the primary way to characterize the interaction of fluids with solid surfaces. This can be expressed with the homonymous equation

\[
\cos \theta_{eq} = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}},
\]

that relates the three surface tensions – \(\gamma_{SG}\), \(\gamma_{SL}\) and \(\gamma_{LG}\) for the solid-gas, solid-liquid and liquid-gas interface respectively – with the equilibrium contact angle \(\theta_{eq}\) (Fig. 1a) [15,18].

Surface tension is defined as the Gibbs free energy per unit surface area [16] at constant temperature, pressure, and chemical potential, whose minimum determines the shape of the interface. A curved interface is mathematically described by the Young-Laplace equation [41] and gives rise to a pressure jump across the two fluids. The equilibrium shape of a fluid on a planar substrate results from the balance between interfacial and gravitational forces, which is expressed by a characteristic length scale, the capillary length \(l_c = \sqrt{\gamma / \rho g}\) (typically 1 mm) where \(\rho\) is the density of the fluid and \(g\) is the gravitational acceleration. The three surface tensions uniquely define the angle of contact for the
considered system, which is used to characterize the static wetting properties of a surface. For \( \theta_{eq} = 0 \) the fluid wets completely the surface, while for \( \theta_{eq} > 0 \) only partially. If the size of the droplet is smaller than the capillary length, then the droplet assumes a spherical cap geometry.

Contact angles on flat surfaces can be measured with sessile drop, captive bubble and Wilhelmy plate methods \([18,21]\). In the sessile drop method (Fig 1a, left) a droplet of fluid is dispensed on a surface and the goniometric angle is measured directly from a magnified image of the droplet at equilibrium. In the captive method the droplet, which is usually lighter than the surrounding fluid, is held captive from a top surface. With the Wilhelmy plate method a sample with a well-defined geometry is dipped in the liquid of interest (Fig 1a, right) and the capillary force is directly measured with a microbalance.

The surface tension of two immiscible fluids, e.g. a water-air or water-oil interface, can be measured with different methods, such as the ring tensiometer, spinning drop, pendant drop, and Wilhelmy plate \([4,41]\). These methods can measure values of surface tension down to a few mN/m. For lower surface tension systems alternative methods based on confocal microscopy \([42]\) or microfluidics \([43]\) are required.

In computer simulations utilizing molecular dynamics or lattice Boltzmann methods the surface tension is often an input parameter. However, this is not the case for all multiphase and multicomponent models on the market. Furthermore, in the case of complex fluids such as suspensions or mixtures, the surface tension has to be obtained from simulations. Often the classical setup of Laplace is used, where a droplet is suspended in a secondary fluid and the surface tension can be obtained from the pressure difference between the inside and outside of the droplet together with the curvature of the interface. Alternatively, the surface tension can be directly obtained from integration of the pressure tensor across the fluid-fluid or fluid-solid interface \([44–48]\).

Young’s equation (Eq. 1) assumes the contact angle to be in thermodynamic equilibrium on an ideal solid surface – smooth, insoluble, chemically homogeneous, nonreactive, and non-deformable \([49]\). In most experimental situations, chemical or topological heterogeneities are present. This becomes clear when we observe an out-of-equilibrium situation, such as a droplet on a tilted surface (Fig 1b). The droplet first deforms and eventually starts moving downhill with different values for the advancing (\( \theta_{adv} \)) and receding (\( \theta_{rec} \)) contact angles. The difference between the two states is known as contact angle hysteresis (\( \Delta \theta \)):

\[
\Delta \theta = \theta_{adv} - \theta_{rec}.
\]

Contact angle hysteresis is omnipresent in nature – even for single crystal structures like mica or graphene – and is relevant for many technological applications, e.g. dip coating, painting, and immersion lithography \([9]\). Contact angle hysteresis is the result of the interaction of the three-phase contact line with macroscopic (micrometer) and microscopic (nanometer) sized defects, where the local contact angle may assume values different from the macroscopic \( \theta_{eq} \). Contact angle hysteresis has been used to characterize surface heterogeneities \([17,18,20,49,50]\). As an example, Bormashenko et al. studied contact angle hysteresis on different polymer substrates, finding that the pinning force of the contact line correlates with the dielectric constant of the polymer substrate. On a macroscopic level, this represents the level of polarity of the polymer, which correlates with the surface energy of the substrates, which in turn is correlated to the measured contact angle. Numerically, contact angle
hysteresis has been studied in the context of droplets on heterogeneous substrates or capillary filling using lattice Boltzmann \([51–54]\) and molecular dynamics simulations \([55–57]\).

**Dynamic contact angle**

Wetting – static and dynamic – is the result of microscale interactions of fluid molecules with a surface. The specific properties of the involved fluids and surface result in macroscopic effects which are typically characterized by experimentally accessible parameters such as viscosity, surface tension, wetting speed and (dynamic) contact angle. However, this indirect quantification of the underlying microscopic processes complicates the development of models and leaves still many questions unanswered. Computer simulations might be used to complement experiments since they allow to model the impact of varying molecular interactions or microscopic surface properties such as roughness, elasticity, charges, or hydrophobic/hydrophilic interactions individually and to investigate the effect of these microscopic quantities on macroscopic measurements \([51,53,58–63]\).

The motion of a contact line over a surface can be studied experimentally with passive and active methods. In spontaneous wetting, a droplet spreads on a flat surface and the dynamic contact angle \(\theta_D\) or the contact line radius are measured as a function of time. In force driven wetting, the contact line is moved by external forces and dynamic contact angles are measured as a function of the speed \(v\) of the moving contact line. The scaling behavior of a moving contact line is often expressed with dimensionless quantities: the Reynolds number \(Re = vL/\mu\), where \(L\) is a characteristic linear dimension and \(\mu = \eta/\rho\) the kinematic viscosity, represents the ratio between inertial forces and viscous forces; the Capillary number \(Ca = v\eta/\gamma\), where \(\eta\) is the dynamic viscosity and \(\gamma\) the surface tension, describes the relative effect of viscous forces and capillary forces.

As a general outcome of many reported experiments, the dynamic contact angle shows a directional and time-dependent character, with values for the advancing and receding contact angles depending on the velocity of the moving contact line (Fig. 2a). This dependency suggests that the process must be thermodynamically irreversible and therefore dissipative \([17,20]\). Yet there is still no consensus on a physical model that can describe and integrate the multi-scale aspects of dynamic wetting. The two main approaches to model the dissipation mechanism are the hydrodynamic theory and molecular kinetic theory. The complete treatment of these theories is outside the scope of this paper and we refer to recent reviews for further details \([17,18,20,22]\). Below we outline the basic principles.

**Hydrodynamic theory**

The hydrodynamic theory assumes that the dissipation is caused by the viscous flow within the wedge of liquid near the moving contact line. The system is described at three different scales (Fig. 2b):

- **Macroscopic**, where the conventional no-slip boundary condition is applied and the system is described by the dynamic contact angle \(\theta_D\); **mesoscopic**, where viscous bending of the interface occurs; and **microscopic**, where the fluid is allowed to slip within few molecular layers above a solid substrate with a local microscopic contact angle \(\theta_m\) (\(\theta_m \neq \theta_D\)). The relation between the viscous bending of the interface and the macroscopic contact angle can be expressed by the Cox-Voinov law \([64]\)

\[
\theta_D^2 - \theta_m^2 = 9Ca \ln \left( \frac{L}{l_m} \right)
\]

that relates the macroscopic \(\theta_D\) and microscopic \(\theta_m\) contact angles, the capillary number \(Ca\) and macroscopic \((L)\) (e.g. the capillary length) and microscopic \((l_m)\) length scales. The latter parameter
represents the typical length scale where the no-slip condition breaks. This model, valid for small Capillary and Reynolds numbers \((Ca, Re \ll 1)\) on ideal surfaces, strongly depends on the boundary conditions imposed to the problem.

**Molecular kinetic theory**

The Molecular Kinetic Theory (MKT) describes the contact line motion as a stochastic process. The motion of the contact line is described by individual molecules that hop in a potential well landscape provided by the atoms of the substrate, with equilibrium frequency \(\kappa^0\) and average displacement \(\lambda\). Here the contact angle is defined at a molecular scale (Fig. 2c) and has the same value as the macroscopic contact angle \((\theta_D = \theta_m)\). The velocity-dependence can be interpreted as being the result of a perturbation of the equilibrium process, which gives rise to surface tension forces. An approximate solution is given by the relation

\[
v = \kappa^0 \lambda^3 \gamma (\cos \theta_{eq} - \cos \theta_D) / k_B T = \gamma (\cos \theta_{eq} - \cos \theta_D) / \xi, \tag{4}
\]

where \(\xi = k_B T / \kappa^0 \lambda^3\) is the friction coefficient and has the same unit as dynamic viscosity (Pa·s).

**Comparison with experiments**

Several authors [17,18,22,65] have reported studies on specific wetting geometries in order to test the proposed models. For example, data can be obtained by pushing fluids into capillaries, or by dip coating substrates into a pool of liquid at different velocities. In most of the cases, both models can reproduce the data for low Capillary numbers, despite the fact that the models are based on different physical mechanisms.

A limitation for the hydrodynamic model is to have accurate information about \(\theta_m\), which is typically assumed to be either \(\theta_m = 0\) (a totally wetting fluid with a precursor film) or \(\theta_m \approx \theta_{eq}\). The associated length scales are typically \(L / L_m \approx 10^4\). For the molecular kinetic model, the value of the equilibrium frequency may vary by several orders of magnitude, while \(\lambda\) is usually of the order of a few nanometers. Values for the contact line friction are found to be higher than the dynamic viscosity of the fluid.

Furthermore, the MKT model lacks a link to the hydrodynamics of the system. The main limitation of both models is the inability to predict the parameters for a given solid-liquid system. The key parameters usually have to be treated as adjustable parameters and obtained from experiments by curve-fitting procedures.

For high Capillary numbers, there is a maximum speed for the contact line motion and wetting transitions may occur, such as the deposition of liquid films, breakup of liquid drops, or entrainment of air bubbles. This topic has been recently reviewed by Snoeijer et al. [22]. They conclude that at low wetting speeds the dissipation is mainly dominated by thermal activation and at higher speeds by hydrodynamics. Moreover at very short timescales the spreading of droplets on partially wetting surfaces is dominated by inertial effects rather than viscous effects, and is independent of substrate wettability [66].

Wetting is a complex problem because phenomena at different length and timescales need to be coupled. Models based on hydrodynamic and molecular kinetic theories can describe equally well the experimental data, although the underlying physical mechanisms are different. The difficulty to access microscopic scales makes it difficult to prove or disprove one model or the other. Thus new experimental techniques accompanied by reliable numerical tools are needed. The study of wetting on single colloidal
particles trapped at fluid-fluid interfaces may offer novel avenues where small scale effects are dominant and quantitatively observable.

PARTICLES AT FLUID-FLUID INTERFACES: STATIC CONTACT ANGLE

In the previous section we focused on unanswered questions about the origin and scaling relationships of dynamic wetting. One important challenge is to gain access to the small scale of a moving contact line. This problem may be addressed by studying wetting on single colloidal particles at fluid-fluid interfaces. In the next sections we outline experimental and numerical techniques to study static and dynamic contact angles on single particles at fluid-fluid interfaces, including a new method that we suggest based on magnetic tweezers.

A particle trapped at a fluid-fluid interface can be described by Young's equation (Eq. 1), where now the three phases are the surface of the particle and the two fluids. For a water-air interface, if the contact angle is $0 \leq \theta \leq 90^\circ$ then the particle is more immersed in the water (hydrophilic), while for $90^\circ \leq \theta \leq 180^\circ$ the particle is more exposed to the air (hydrophobic) (Fig 1c).

The energy of adsorption of such a particle can be calculated by considering the contribution of the surface free energies of the three phases [3]. This yields:

$$\Delta E = -\pi R^2 \gamma (1 - |\cos \theta_{eq}|)^2,$$

where $R$ is the radius of the colloid, $\gamma$ is the surface tension of the fluid-fluid interface and $\theta_{eq}$ is the three phase contact angle at equilibrium, as sketched in Fig 1c. This energy is usually much larger than the thermal energy. As an example, for a particle of 1 micrometer radius at a water-decane interface ($\gamma \approx 50 \text{ mN/m}$), with $\theta_{eq} = 90^\circ$, the adsorption energy is about $\Delta E \approx 10^7 \text{ K_B T}$, making the adsorbed state practically irreversible.

The equilibrium contact angle of colloidal particles trapped at fluid interfaces cannot be measured with the same techniques as for planar surfaces. The main differences are the small scales of the system (micro- and nanoparticles) and the presence of an optical discontinuity between the two fluids. Several approaches have been reported in literature and the topic has been recently reviewed by Maestro et al. [7]. Here we will discuss some of the techniques, with focus on single particle methods.

**Experimental techniques for measuring the contact angle of particles at fluid interfaces**

We can distinguish two different approaches: ensemble measurements and single particle based methods. Ensemble measurements deduce an average contact angle from a measurement on a large number of colloids. In many cases the results are obtained with assumptions that can be difficult to verify. For example, in the Washburn technique [23] a powder bed with irregular nanometer-sized particles is put in a capillary and the position as function of time of a fluid adsorbing into the powder is measured. The contact angle is extracted by fitting the data to a model function. The model relies on the pore diameter of the wetted powder, whose physical meaning is matter of debate. In a Langmuir trough experiment [24] pressure and area are measured upon compression of the interface containing the particles. During the process the particles are tightly packed and eventually expelled from the interface.
The contact angle is extracted from the measured critical pressure, assuming no deformation of the interface.

Single particle based techniques have interesting advantages. Ideally the measurements are direct, with minimal assumptions to extract contact angles. Furthermore, a measurement on single particles allows one to investigate small-scale effects and to quantify particle-to-particle variability. In an early report, Mingins et al. [29] directly observed 50 μm silica particles on a water-air interface of a pendant drop and extracted the contact angle from microscope images. Hadjiiski et al. [31] measured the interference pattern of micrometer sized particles on a substrate trapped in a thin film and the value of the contact angle was extracted from the meniscus profile. Horozov et al. [35] developed a similar interferometric technique, but now with a particle bridging a thin film. Preuss et al. [32] glued a colloidal particle onto the cantilever of an atomic force microscope (AFM). In this colloidal probe AFM experiment, the particle is brought into contact with the interface, where capillary forces cause the cantilever to bend. Upon further approach of the probe, it reaches a zero-force position and thereafter forces apply in the opposite direction. Depending on the direction of cantilever actuation, values for the advancing and receding contact angles can be extracted, using the radius of the particle and the difference between the first-contact and the zero-force positions. The contact angle was measured for a 5 μm silica particle at a water-air interface with and without the presence of surfactants.

Paunov et al. [33] developed a Gel Trapping Technique (GTT) to measure contact angles on single nanoparticles with a diameter of 100 nm. The technique uses a thermo-responsive non-adsorbing gellant agent in the water phase. Then a soft polymer (PDMS) is used to replace the oil phase and trap the particles upon solidification, thereafter the mold is analyzed with a scanning electron microscope or AFM [67]. An alternative solidification technique was developed by L. Issa et al. [36]. Particles were spread at a fluid-fluid interface, and after jet-freezing and cracking of the interface, the particles were metal-coated at a specific angle, thus forming a shadow. By measuring the geometry of the shadow with SEM images, it is possible to quantify the contact angle. The technique allows one to measure the contact angle of particles with diameters down to 20 nm. N. Vogel et al. [37] reported a method to study particles at a water-air interface based on polymerization. A monomer is introduced in the gas phase that polymerizes in contact with the water phase. Thereafter the film is analyzed with scanning electron microscopy and the value of the contact angle is extracted.

Maestro et al. compared the contact angle values obtained with different techniques for different particle-interface systems; see Table 1 in reference [7]. Their extensive analysis shows that several parameters influence the measured values, such as particle radius, chemical nature of the surface, charge density, roughness and porosity, fluid properties, and the experimental protocol. The large number of parameters and the lack of an extensive study over a wide range of particle-interface systems make it difficult to predict values for contact angles from a priori knowledge of a system. Moreover, as for planar surfaces, contact angle hysteresis is present and the measured contact angle is an apparent value. Contact angle hysteresis is a dynamic effect and depends on the history of the moving contact line. The abovementioned solidification techniques do not allow studies of such dynamic effects.

Another aspect that strongly affects the behavior of colloidal particles is the shape of the interface. Particle surface heterogeneities may distort the interface at the three-phase contact line, which can be described as a superposition of capillary multipoles, in analogy with electrostatics (capillary charge, dipole, etc.) [68–73]. The overlap of these interfacial deformations result in long-range interactions
between particles at interfaces, thus controlling the assemble into ordered structures. As an example, interfaces with anisotropic curvature may change the particles assembly from an hexagonal (flat interface) to a square lattice (as a result of quadrupolar interactions) [69]. This effect is particularly important for anisotropically shaped objects, which assemble in preferred directions [13,70,74].

Prior to any measurement, particles need to be positioned at the interface. This can be done either by spontaneous adsorption from the bulk fluid or with the use of spreading solvents (typically alcohols) that frequently implies a turbulent flow at the interface [7]. As an example, Table 1 of Maestro et.al. shows that for the same system – 2 µm diameter PMMA particles at a water-air interface, measured with the gel trapping technique – the measured contact angle changes significantly depending on the solvent used – 56 degrees for isopropanol and 29 degrees for methanol. The difference is attributed to the solvent molecules adsorbed to the surface of the particles [75]. Variability may also arise from the dynamic nature of wetting. Initially, the capillary forces and hydrodynamics of a particle adsorbing to a fluid-fluid interface give wetting speeds in the order of a few m/s, while also longer timescale relaxation processes are observed with speeds as low as \(10^{-3}\mu m/s\) [38–40]. Such dynamic wetting effects should be taken into account when extracting values for the contact angle. The capillary adsorption energy (Eq. (5)) depends on the curvature of the interface, but it becomes significant only when the curvature of the interface is comparable with the radius of the particle [76].

Numerical techniques to simulate particles in the vicinity of fluid interfaces

Particles at fluid interfaces have been studied using (semi-)analytical treatment and computer simulations by numerous authors in the past. However, in most cases the hydrodynamic properties of the involved fluids are ignored in order to simplify the problem and to save computing time [71,73,77–82]. While these works have provided a thorough insight of the general behavior of particles at interfaces, in order to understand dynamic wetting properties, they are only of limited applicability: to understand the fundamental origin of wetting a proper treatment of hydrodynamics and the dynamic movement of the contact line or deformability of the interface is required.

Simulation methods which are able to cover the movement of particles and the hydrodynamics of the fluid-fluid interface can generally be classified as hybrid approaches: the particles follow Newton’s equation of motion and can be treated by standard molecular dynamics or discrete element algorithms. The fluids have to be treated on the level of a multiphase or multicomponent solver recovering the Navier-Stokes equation or at least the Stokes equation. Molecular dynamics is a possible method here, but its applicability is limited by the huge computational costs involved [83]. Often diffuse interface models are applied in order to avoid the complicated tracking of the interface and in particular the three phase contact line.

Finally, the particle- and fluid solvers have to be coupled, which needs to be implemented by a consistent treatment of momentum transfer between the fluids and the particle surface on a scale sufficiently smaller than the particle diameter. Typical choices for the flow solver include classical finite element methods [84], dissipative particle dynamics (DPD) and again the lattice Boltzmann method. Algorithms involving the lattice Boltzmann method have been successfully applied to study the formation of particle stabilized emulsions such as Bijels and Pickering emulsions involving spherical [10,85,86] and anisotropic particles such as ellipsoids [87]. Furthermore, these methods have been used
to study particle covered droplets or particles at interfaces under the influence of external fields [13,47,88]. Static wetting effects can be easily controlled by tuning e.g. the surface properties of the particles and parameters such as the particle contact angle are directly accessible from the fluid concentration fields obtained in the simulation [86,89–91].

From a fundamental point of view there is a need to understand the mechanisms underlying dynamic wetting processes, over a wide dynamic range in space and time. The knowledge of dynamic wetting of single particles is important for technological applications in order to be able to predict the behavior of ensembles of particles and to scale up systems. In the next section we will present experimental techniques and numerical models to study dynamic wetting of colloids.

PARTICLES AT FLUID-FLUID INTERFACES: DYNAMIC WETTING

Dynamic wetting plays an important role in the adsorption process of colloids at fluid-fluid interfaces. A description based on capillary forces and hydrodynamics results in exponential relaxation times with typical timescales of µs. Recently much longer timescales – several minutes, hours – were measured [38–40]. These observations call for the development of methods to quantify and model dynamic wetting effects on individual particles over a broad range of time and energy scales, and suitable for a wide range of particle types and fluid properties.

The dynamic nature of wetting can be studied by monitoring the spontaneous adsorption of a particle and by perturbing its equilibrium position (Fig. 1d). This requires the ability to measure the time evolution of the position of a particle with respect to the interface, and an actuation method in order to move a particle out of its equilibrium position. In the following paragraphs we outline experimental and numerical techniques to study dynamic contact angles on single particles at fluid-fluid interfaces. Finally we conclude by discussing the status and future of single particle based experimental techniques, and we propose a method based on magnetic tweezers.

**Experimental techniques**

Kaz et al. [38] studied the relaxation to equilibrium of colloids using digital holographic imaging in combination with optical tweezers (Fig. 3a). They recorded trajectories of micrometer-sized polystyrene particles with different surface chemical properties as they approached and breached a water-decane interface (Fig 3b). Holographic images were generated by illuminating the particles with a laser. The two fluids were index matched and the axial position of the particle was calculated by solving the Lorentz-Mie scattering equation in bulk. Another laser was focused on the back of a high numerical aperture microscope objective, creating an optical trap [92] in order to move the particle towards the interface. With this setup the 3-dimensional position of the particle was resolved with 2 nm spatial resolution and sub-millisecond time resolution.

The initial approach trajectory can be explained by the hydrodynamic interaction of the particle with the interface (Fig. 3b). A particle in a low salt water solution (1mM) reaches a steady level in proximity of the interface, while for a higher value (100 mM) the particle breaches the interface. This is attributed to the electrostatic barrier that arises when charged particles approach an interface between a high dielectric (water) and a low dielectric medium (decane) [8,93]. After a sudden jump the particle follows a
logarithmic trajectory (Figure 3b). The position of the interface, and so the apparent contact angle, is computed from the relative position of the particle right before the snap-in process.

The results were interpreted with a Molecular Kinetic Theory [17], as described in the section Contact angles on planar substrates. The model describes the motion of the contact line as a stochastic process. Local surface heterogeneities trap fluid molecules in a potential well, whose energy is modified by a driving capillary force. The velocity of the contact line is related to the rate at which it hops over surface defects with average area $A$. This model is able to describe the observed logarithmic trajectories for times greater than 10 ms over three decades (Fig 3c). Particles with different surface functional groups show the same logarithmic behavior (Fig 3d), providing similar values for surface defect areas in the order of a few nm$^2$, but with different relaxation rates. In a follow up paper [40] Wang et al. further investigate the nature of these defects, demonstrating that the contact line is pinned to topological defects rather than charged patches. Interestingly, they observed a fast relaxation behavior for PMMA particles approaching from the decane phase rather than from the water phase, showing the complex nature of wetting.

Chen et al. [39] used a colloidal probe AFM to study the time-dependence and force of the early snap-in stage of a particle adsorbing to a water-air interface (Fig. 4a). Experiments were performed with silica particles of different radii, in a hydrophilic state as well as with a hydrophobic coating. The position of the interface and the snap-in time were determined by the deflection of the cantilever using a similar approach as Kaz et al. [38].

Chen et al. observed two relaxation timescales: a slow logarithmic relaxation for $t \sim s$ (Fig 4b), in agreement with [38]; and a fast relaxation for $t < ms$ (Fig. 4c). At this short timescale the fast adsorption is characterized by damped oscillations with the same frequency as the resonance frequency of the cantilever. The snap-in time, $t_s$, defined as the time for the particle to reach a steady position, was similar for both hydrophilic and hydrophobic particles. A characteristic timescale of the snap-in process can be obtained by considering the particle momentum change and capillary forces. This results in $\tau \sim (\rho_p R^3/\gamma)^{1/2}$, where $\rho_p$ and $R$ are the density and the radius of the colloidal probe respectively. Measurements of $t_s$ for particles with different radii and hydrophobicity confirmed this relation, proving that the snap-in time is dominated by inertia rather than particle wettability. As the authors pointed out, the scaling behavior is analogous to the initial spreading of droplets on flat surfaces [66], where the early-stage spreading ($t \sim \mu s$) is dominated by inertia rather than surface wettability. From force measurements, Chen et al. estimated snap-in forces in the order of a few $\mu N$, with a linear relationship between the snap-in force and the radius of the colloid, which is larger for hydrophilic than for hydrophobic particles.

**Numerical techniques**

Numerical studies relevant to dynamic wetting are very limited, but cover topics such as interface functionalization, the adsorption and desorption behavior of single particles at a fluid interface, capillary interactions between several (anisotropic) particles, or the impact of external fields on the structuring and movement of particles at interfaces.

An example for the functionalization of colloidal particles at a fluid interface is based on molecular dynamics simulations of Ehlinger et al. [83]: they demonstrate that hydrophobic colloidal particles can be placed crossing a lubricating gas layer between two liquid phases. Under a shear flow, these particles act
as bearings and allow to substantially reduce the friction as compared to a pure fluid-fluid interface.

Razavi et al. [94] also investigated the rotational dynamics of particles using molecular dynamics and their findings are particular relevant for the example of a possible measurement technique based on magnetic tweezers as provided in the last section of this article.

DeGraaf et al. presented a Langevin dynamics study [95] of adsorption trajectories and free energy separatrices for colloidal particles with arbitrary shape. However, hydrodynamics is not included in the model. Günther extended these studies by lattice Boltzmann simulations of single ellipsoidal particles adsorbing to an interface and demonstrated that the deformability of the interface has an influence on the exact shape of the adsorption trajectories [87,91]. Davies et al. on the contrary have studied in detail how an anisotropic particle detaches from an interface by dragging it off with a constant force. From such simulations a precise measurement of detachment energies is possible [96].

Joshi and Sun studied the dynamic wetting properties of evaporating droplets covered by particles using lattice Boltzmann simulations [97] and very recently Frijters et al. demonstrated that a dynamic change of contact angles in particle stabilized emulsions might be a possible route to the self-assembly of well-defined filters or catalysts [87].

Davies et al. [13,98] studied the behavior of magnetic ellipsoidal particles under the influence of a magnetic field using the lattice Boltzmann method. The particles undergo a magnetic torque and deform the interface, leading to capillary interactions. They show a novel bottom-up method to facilitate self-assembly structure of ellipsoidal particles at the interface.

A relevant example for our discussion – that allows a direct comparison with the experimental results presented in [38,39] – is provided by Colosqui et al. [99]. In this paper, the adsorption of a particle to a fluid-fluid interface is analyzed theoretically and by molecular dynamics simulations. The motion of the particle towards equilibrium is driven by the minimization of the surface free energy. The adsorption dynamics is modulated by introducing local energy minima and maxima in the potential energy landscape, expressed by

\[ U(z) = U_{s}(z) + \frac{1}{2} \Delta U \sin(\lambda z + \phi) \]  

(6)

where \( z \) is the center-to-interface distance, \( U_{s}(z) \) is the interfacial free energy (Eq. 5), \( \frac{1}{2} \Delta U \) is the amplitude of the perturbation, \( l = 2\pi/\lambda \) is its wavelength and \( \phi \) is a variable phase. These perturbations (with \( l \ll R \)) are interpreted as microscale surface heterogeneities. The forward and backward hopping of the contact line from these metastable states is described with Kramers’ theory [100]. The solution of the equation of motion is described by three independent physical quantities; i.e., the characteristic hop length, the trajectory amplitude (determined by the initial separation from equilibrium position), and a characteristic hop time. The model predicts different relaxation regimes, from fast exponential relaxation – for a perfectly smooth 1 \( \mu m \) radius particle the decay time is 0.1 \( \mu s \) – to slow logarithmic or exponential relaxations in the vicinity of the equilibrium position, recovering the same behavior as for Kaz et al. [38].

As stated by the authors, their model based on Kramers’ theory is mathematically similar to the MKT model presented in [38], and both can describe the slow logarithmic relaxation. The difference lies in the underlying physical assumptions. The MKT assumes that dissipative forces – determined by a characteristic hopping time over atomic sized defects – are driving the particle toward equilibrium, while
Kramers’ theory assumes that the driving force is related to a quasi-static process of surface minimization, determined by geometrical features on the particle surface. These findings demonstrate that the wetting dynamics of a particle adsorbing at a fluid-fluid interface is dominated by surface heterogeneities, but as for planar substrates, a consensus on the underlying physical mechanisms is still lacking.

**Future perspectives**

Wetting on single particles can be studied with optical tweezers and colloidal probe AFM. These techniques are suitable to study relaxation to equilibrium of colloids with different surface functionalization and sizes (1 – 100 \( \mu m \)), and for different systems (e.g. water-oil and water-air interfaces). To move a particle out of its equilibrium position forces normal to the interface or torques can be applied. Forces in the range of several hundreds of pN to \( \mu N \) are typically required. Optical tweezers is a “contact-free” actuation method that can apply both translational and rotational forces. Vertical forces range from 0.1 pN to hundreds of pN, but for such high forces a high intensity laser is required, which might heat the sample changing the local properties of the interface or even melt or destroy the particle. Torques can only be applied to optically anisotropic particles [101], in the range of \( 1 - 10^5 \) pN·nm. AFM can apply translational forces from a few pN to hundreds of nN, depending on the cantilever spring constant [92,102], but it cannot apply torques.

Another technique that allows to apply forces and torques is magnetic tweezers. Magnetic tweezers use magnetic fields and magnetic field gradients to manipulate magnetic particles [14,92,103]. A magnetic particle in a magnetic field gradient experiences a translational force that depends on the magnitude of its magnetic moment and of the gradient. In a spatially uniform, but rotating, magnetic field, a magnetic particle does not experience a translational force but experiences and exert a torque. Magnetic fields can be controlled by electrical currents which gives the possibility to create magnetic fields with different magnitudes and orientations (Fig. 5c). Particles can be imaged using conventional digital microscopy techniques to resolve their position. Typical forces range from few pN to tens of nN [92] depending on the magnetic properties of the particles and the source of the magnetic fields. Typical torques range from \( 10 - 10^7 \) pN·nm (for particles with a magnetic moment between \( 10^{-16} - 10^{-13} \) A·m\(^2\) and magnetic fields of \( 0.1 - 100 \) mT [14,104]).

The main advantage of magnetic tweezers is the possibility to actuate the probe with 6 degrees of freedom (3 translational and 3 rotational). By measuring the translation and angular orientation of the particle it is possible to measure the response of the system upon external stimuli. This method has been exploited for example for interfacial microrheology studies [105,106]. Translation can be resolved with microscopic techniques; rotation can be resolved if optical features are present on the rotating object, such as holes on a flat disk [107], or fluorescent tags on a magnetic particle [14,104].

Here we propose an experiment based on magnetic tweezers to study wetting at small scales, as described in Fig. 5a-d. A magnetic particle trapped at a fluid interface is interrogated with different magnetic torques. From the study of the particle angular orientation as function of time we expect to observe different behaviors (Fig. 5d). First, the particle will deform the interface (region I) until the torque is sufficient to overcome the contact-line pinning, which depends on the particle surface properties and fluid surface tension. Then, for higher torques we expect a displacement of the contact line at different rotational speed (region II and III).
Contact-line pinning energies and contact angle hysteresis can be quantified as a function of microscale surface features, e.g. roughness and chemical properties, and different combinations of fluids. The quantification of the deformation of the interface for a known torque can be used to determine the surface tension, or to study capillary-dipole interactions. Moreover, wetting dynamics can be studied on a microscale level for different Capillary numbers, and a large number of parameters.

These experiments can be accompanied by computer simulations. For example, Razavi et al. [94] use molecular dynamics simulations to investigate the effect of localized features on the rotational dynamics of nanoparticle straddle at fluid-fluid interface, based on Kramers’ model. They show the presence of long-lived metastable states where the particle remains locked in angular orientations. Alternatively, simulations based on combined lattice Boltzmann and molecular dynamics methods as outlined above could be applied. Figure 6e shows an example snapshot from such a simulation: a magnetic particle is trapped at a fluid-fluid interface and a constant torque is applied. Due to the resulting rotation of the particle and the interaction of the particle surface with the fluids, the interface deforms and the dynamic contact angle on the particle surface can be measured. The advantage of this kind of simulations is that parameters such as surface tension, particle surface morphology or time dependence of the magnetic field can be varied systematically and independently.

The force needed to drive particles out of equilibrium depends a.o. on the presence of contact line pinning and surface tension. A water-decane interface has a surface tension of roughly $50 \, \text{mN/m}$, or $10 \, k_B T/\text{nm}^2$, which represents a large energy density. Therefore, to make all modes of particle motion accessible in a magnetic tweezers experiment, it is preferred to have high magnetic fields and particles with high magnetic moments available, ideally with a wide variety of particle surface properties such as roughness and surface functionalization.

Another interesting approach is to use anisotropic particles. Although many experimental studies have been done with spherical particles, computer simulation on particles with different shapes (e.g. ellipsoids, cylinders, dumbbells, etc.), or surface properties (e.g. Janus particles), or a combination of shape and surface properties (e.g. Janus ellipsoids), reveal unique properties that may be exploited for particle self-assembly at interfaces or as a platform for the design of novel colloid-based materials.

**CONCLUSIONS**

The equilibrium shape of a fluid interface and the displacement of a fluid over a surface are the result of fluid molecules interacting with another phase. The specific properties of the involved fluids and surface result in macroscopic effects which are typically characterized by experimentally accessible parameters such as viscosity, surface tension, wetting speed and dynamic contact angle. However, these parameters give only indirect information about the underlying microscopic and molecular-scale processes, and this indirectness complicates the development and validation of model descriptions. Studying the wetting of single colloidal particles trapped at fluid-fluid interfaces may offer novel avenues, where small scale effects are dominant and quantitatively observable.

In this paper we have presented novel methodologies to study wetting, focusing on experimental and numerical techniques based on single colloidal particles at fluid-fluid interfaces. We concluded by proposing an experiment based on magnetic tweezers, where magnetic particles at a fluid-fluid interface are interrogated with induced magnetic torques. With single particle based methodologies, pinning
energies and wetting hysteresis may be studied as a function of morphological and chemical surface features for particles at different fluid interfaces, in order to test different models under a wide range of parameters. The quantification of interface deformation for a known torque can be used to quantify surface tension, or to study capillary-dipole interactions. Moreover, wetting dynamics can be studied on a microscale level for different Capillary numbers and fluids. Computer simulations based on combined lattice Boltzmann and molecular dynamics methods might be used to complement experiments since they allow to model the impact of varying molecular interactions or microscopic surface properties such as roughness, elasticity, charges, or hydrophobic/hydrophilic interactions individually.

Dynamic wetting effects play a role in many applications, including bioanalytical tools where aqueous sample fluids come in contact with solid surfaces and secondary phases. Wetting effects at short and long timescales are particularly apparent in the upcoming generations of lab-on-a-chip systems, where miniaturization implicates very large surface-to-volume ratios, particularly in systems where small droplets or colloidal particles are used for sample manipulation, target extraction, purification, detection, etc. We expect that the development of new experimental techniques accompanied by reliable numerical tools to study dynamic wetting effects on colloidal particles at micro- and molecular scale, will help scientists and engineers form diverse disciplines to tackle a wide range of problems and develop new applications.

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REFERENCES


Macroscopic surface

Colloid at fluid-fluid interface

Figure 1

Static wetting

Dynamic wetting
advancing
$v > 0$
receding
$v < 0$

$\Delta \theta = \theta_{\text{adv}} - \theta_{\text{rec}}$

(a) (b) (c)

Figure 2
Figure 4

(a) 100 µm

(b) Step-motor

Capillary

Air-water interface

Particle

Cantilever

Laser

Photodetector

\[ D(\mu m) \]

\[ R = 60 \mu m \]

\[ f \sim 150 \text{ Hz} \]

\[ f \sim 230 \text{ Hz} \]

\[ f \sim 5 \text{ kHz} \]

\[ f \sim 5 \text{ kHz} \]
Figure 5

(a) and (b) show the microscope objective and electromagnets, respectively.

(c) illustrates the setup with the microscope objective and electromagnets.

(d) depicts a graph showing the contact-line pinning and increasing torque over time.

(e) illustrates the contact-line pinning under increasing torque.
FIGURE 1. Wetting at different scales. On a macroscopic scale (a) static and (b) dynamic contact angles have been studied by placing a droplet on a planar substrate or by dipping a surface into a fluid. On a microscopic scale (c) static and (d) dynamic wetting are being studied using colloidal particles at fluid-fluid interfaces.
FIGURE 2. Dynamic wetting. (a) Velocity-dependence of contact angle on partially wetting substrates; the jump at zero velocity corresponds to contact angle hysteresis. Modeling of an advancing contact line on a planar substrate with (b) a hydrodynamic theory and (c) molecular kinetic theory. In (b) the contact line is described at three different scales: macroscopic, mesoscopic and microscopic, with $\theta_D \neq \theta_m$. In (c) the system is described at a molecular level as a thermally activated process with $\theta_D = \theta_m$. (Figures after [17,18]).
FIGURE 3. Study of relaxation to equilibrium of particles at a water-decane interface, as reported in [38]. (a) Sketch of the experimental setup: an optical trap is used to bring a particle towards the interface and its height is measured using holographic imaging microscopy. (b) Approach curves of 1.9-µm-diameter polystyrene particles at low and high salt concentrations. The position of the interface is determined from the sharp transition when the particle breaches the interface. (c) Trajectory of a particle relaxing towards equilibrium, showing a logarithmic relaxation behavior. The red dotted line is a fit obtained according to the MKT model. (d) Particles with different surface functionalization show similar logarithmic trajectories, but different relaxation rates. Reprinted and adapted by permission from Macmillan Publishers Ltd: Nature Materials (Ref. [38]), Copyright (2012).
FIGURE 4. Study of the snap-in dynamics of a particle at a water-air interface using a colloidal probe AFM, as reported in [39]. (a, top) Scanning electron micrograph of a glass particle glued onto a cantilever and (b, top) schematic of the colloidal probe AFM setup. The probe approaches the interface and the deflection of the cantilever determines the particle surface-to-interface distance $D$. (a, bottom) Distance $D$ versus time for a hydrophilic (black-squared dots) probe and a hydrophobic (gray-rounded dots) probe. At long time scales ($t = 0$ to $t = 6$ s) both curves show a slow logarithmic relaxation. (bottom, b). At intermediate time scales, damped oscillations are observed due to the excitation of capillary waves upon contact of the particle with the drop surface (bottom, c) At short time scales ($t = 0$ to $t = 3$ ms) a fast wetting process is observed, which is independent of particle wettability. Reprinted with permission from Ref. [39]. Copyright (2012), AIP Publishing LLC.
FIGURE 5. Proposal to study dynamic wetting in an out-of-plane particle rotation experiment. (a) A magnetic particle with radius $R$ is trapped at a fluid-fluid interfaces; optical labels (e.g. fluorescent nanoparticles) on the particle surface allow for orientation tracking. The magnetic moment $\mathbf{m}$ and magnetic field $\mathbf{B}$ are aligned and normal to the interface. (b) In the presence of a magnetic field parallel to the interface the particle experiences a torque. We define the particle angular orientation $\varphi_p$ as the angle between the magnetic moment and the vertical axis $z$. (c) Sketch of a 3-pole electromagnet setup combined with digital optical microscopy. (d) Sketch of hypothetical outcome of an out-of-plane rotation experiment. Particle orientation as a function of time, for increasing applied torques. Below a wetting threshold, the particle deforms the interface but cannot freely rotate, so the magnetic moment cannot align with the field (region I); above the wetting threshold, dynamic wetting takes place and the three-phase contact line is displaced over the particle (regions II and III). (e) Snapshot of a numerical simulation of a particle at a fluid-fluid interface exposed to a constant torque mimicking a rotating magnetic field. The deformation of the interface due to the interactions between particle surface and fluids can clearly be observed.