Contact Angles and Contact Lines Around Particles at Isotropic and Anisotropic Liquid Interfaces

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CONTACT ANGLES AND CONTACT LINES AROUND PARTICLES AT ISOTROPIC AND ANISOTROPIC LIQUID INTERFACES

A Dissertation Presented

by

NESRIN SENBIL

Submitted to the Graduate School of the University of Massachusetts Amherst in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

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Department of Physics
CONTACT ANGLES AND CONTACT LINES AROUND PARTICLES AT ISOTROPIC AND ANISOTROPIC LIQUID INTERFACES

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To Pelin.
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ABSTRACT

CONTACT ANGLES AND CONTACT LINES AROUND PARTICLES AT ISOTROPIC AND ANISOTROPIC LIQUID INTERFACES

SEPTEMBER 2015

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Liquid interfaces, capillarity and self-assembly of particles at interfaces are important in nature and technology. When a particle is adsorbed to a liquid interface, the contact line of the particle with the liquid interface and the associated contact angle are the crucial parameters that drive assembly of the particles. We looked at how the shape of the liquid interface and the shape of the particle affect the contact angle and the shape of the contact line. We used millimeter-sized PDMS-coated glass spheres and measured the contact angles at isotropic (planar) and anisotropic interfaces (saddle and cylindrical in shape). Anisotropy of the liquid interface is defined by the deviatoric curvature $D_0$. We look at the apparent advancing and receding contact angles ($\theta_a$, $\theta_r$) separately. We found that as the anisotropy of the interface, $D_0$, increased from 0 to 0.22mm$^{-1}$, the apparent receding angle, $\theta_r$, decreased from 101° to 80°. Over the same experiments, $\theta_a$ remained fixed at 109°. As $D_0$ increases, we also find that the contact line around the sphere deforms. We make analogy to electrostatics to describe the shape of the contact line.
in terms of multipole moments. We measured that as $D_0$ increased, the magnitude of the quadrupolar moment ($z_2$) increased and $\theta_R$ decreased. Magnitudes of $z_2$ measured in our experiments agree with previous predictions when capillary force is zero. We also measure the $z_2$ with applied capillary force. However, there is no theory to compare it. To our knowledge, this is the first time that quadrupolar deformation of contact line around a particle is observed and measured directly. Moreover, we showed that advancing and receding contact angles of anisotropic shaped solids, such as cylinders, differ at a planar interfaces, which we attribute to the deformation of the contact line. Our results bring a new perspective to contact angles, showing that the advancing and receding angles depend on liquid-interface geometry, which had not previously been appreciated. Thus, our results are broadly important for capillarity and self-assembly related problems.
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75: Separation between two spheres at times separated by approximately 10 min. Both spheres are PDMS-coated glass, $a=3.2\text{mm}$. Free sphere is on the left and rod-attached sphere is on the right.

76: Contact angles as the separation increases in time.

77: Height difference of left and right sides of the contact line shown for the free sphere (red) and the rod-attached sphere (blue). In this plot, a positive value of l-r corresponds to a tilt in the clockwise direction.

78: Interface shape between the two spheres in this image is analyzed. This image is the data point at $d=21\text{mm}$ in the figure above.

79: Plot of interface shape between spheres from Figure 78. The purple line shows the result of the fit to the equation described in the text.
CHAPTER 1

INTRODUCTION

In the last century, research on particle suspensions and emulsions has highly increased due to their existence in nature and use in technology, with examples such as crude oil recovered from ground, blood, ink, paint and dairy products(1-3). Particle size scales in those examples range from nanometer to millimeter(4-6). As an example of millimeter sizes, assembly of mosquito eggs and liquid marbles of aphids can be given(7, 8). Directing assembly of different sizes of particles can be done at liquid interfaces by inducing curvature.

For progress in many of the above applications, it is important to study interactions among particles at liquid interfaces (9). When a particle is placed to a liquid/liquid interface, whether it stays at the interface or not is due to many reasons such as interfacial tension of the liquid and surface properties (chemistry, surface roughness) of the particle. In fact, we observe such behaviors in nature; insects (which might be viewed as active particles) walk on the lakes or grab air bubbles into the water to use it(10-12). Moreover, these properties are used in technology to control wetting of liquids on solids and make self-cleaning, self-drying, and de-icing surfaces(1-3, 13-18).

1.1 Liquid Interfaces

In this section of this chapter, basic information of interfacial tension and Laplace pressure is given and particle interactions at liquid interfaces are described.
1.1.1 Interfacial Tension:

Liquid is a dense state of molecules. When a particle is placed at a liquid interface, the liquid applies a tangential force to the particle’s surface. This force per unit length is called interfacial tension or, interfacial energy with a unit of energy per area. Interfacial tension (\(\gamma\)) is simply the energy that must be supplied to increase the interfacial area by one unit, and it is an intrinsic property of the liquid and the surfaces. This property of the liquid makes the solid objects to be able to stay at the surface of the liquid. That is how some insects can walk on the water and particles denser than water can stay at the surface(10, 19).

1.1.2 Shapes of Liquid interfaces/Curvatures:

Principal curvatures (\(c = 1/R\), where \(R\) is the radius of curvature) determine the shape of a given surface. At a given point, the maximum and minimum curvatures are the principal curvatures of that point. Principal curvatures are measured along two directions on the surface that are perpendicular to each other. Let us call those two principal curvatures as \(c_1\) and \(c_2\). Figure 1 shows principal curvatures of a surface:
Surface shapes may be parameterized by three different combinations of these two curvatures; mean curvature ($H$), Gaussian curvature ($G$), and deviatoric curvature ($D$).

Mean curvature is the half of sum of the two principal curvatures. Its unit is 1/length and defined as:

\[
H = \frac{c_1 + c_2}{2}
\]
Gaussian curvature is the product of the two principal curvatures and has a unit of 1/length\(^2\). Gaussian curvature is used to define whether a surface is locally convex/concave or saddle (Figure 2).

1.2 \[ G = c_1 * c_2 \]

On the other hand, Dviatoric curvature is an indicator of anisotropic shapes. It is half of the difference in principal curvatures;

1.3 \[ D = \frac{c_1-c_2}{2} \]

According to this definition, symmetric shapes have zero deviatoric curvature and other shapes have non-zero deviatoric curvature. For instance, flat and spherical surfaces have \( D = 0 \), and saddle and cylindrical interfaces \( D \neq 0 \).
Figure 2: A saddle, cylindrical and spherical shapes are shown. Saddle, cylindrical and spherical shapes have negative, zero and positive Gaussian curvatures respectively. (Image from Wikipedia entry: Gaussian Curvature)

1.1.3 Laplace Pressure:

The Laplace pressure is the pressure difference between two immiscible static fluids such as water and oil. When a drop of oil is placed inside a water bath, the oil makes a spherical shape to minimize its surface energy. In order to minimize the surface area and interfacial energy, the interior fluid is slightly compressed by a pressure defined as the Laplace pressure. Thus, pressure difference is calculated as;

\[
\Delta P = P_1 - P_2 = 2H\gamma
\]
When the shape in between two liquids is spherical such as in water/oil interface two principal curvatures are equal to each other; \( c_1 = c_2 = 1/R \). Thus,

\[
H = \left( \frac{1}{R} + \frac{1}{R} \right) = \frac{2}{R}, \quad \Delta P = \frac{2\gamma}{R},
\]

where \( R \) is radius of the sphere. Now assume that the interface between two fluids has an arbitrary shape as seen in figure 3.

![Figure 3: Arbitrary interface between any liquids 1 and 2.](image)

General form of the Laplace Equation is,

\[
2H\gamma = P_1 - P_2
\]

where,

\[
2H = \nabla u\left\{ \frac{\nabla u}{\sqrt{1 + |\nabla u|^2}} \right\} \quad \text{and} \quad \nabla u = e_x \partial_x + e_y \partial_y
\]

Thus, the Laplace pressure at any point on the interface can be found with the information of the mean curvature at that point. Moreover, to make pressure measurement of a bubble inside a liquid bath such as water as seen in the figure 4 one can balance the Laplace pressure with the hydrostatic pressure from gravity;

\[
P(R) = P_0 + \rho gh + \frac{2\gamma}{R}
\]
where $\rho$ is density of the liquid, $g$ is the gravitational acceleration and $h$ is the depth of the bubble (or length of the cylinder dipped into the liquid).

One can find shape of the liquid interface from the Laplace Pressure. In mechanical equilibrium, the sum of the Laplace pressure and external pressures (electrostatic, gravity, etc.) must be constant otherwise the fluid will flow. Thus, in the absence of external forces, the mean curvature $H$ is uniform.

$1.9$ \[ H = \frac{1}{2} \nabla^2 u(x, y), \]

Assuming $\nabla u(x, y) \ll 1$. As an example, the shape of a heavy disc sitting at an interface is determined by $\frac{1}{2} \gamma \nabla^2 u + (g \Delta \rho) u = 0$, where the second term describes the gravitational pressure and $\Delta \rho$ is the difference of the densities of the two fluids.

The solution to this problem depends on a single characteristic length, known as the
capillary length and defined as $L_c = \sqrt{\gamma/\rho g}$. In our experiments capillary length is 2.7mm.

1.1.4 Capillary Interactions of Particles at Liquid Interfaces

When the gravitational force on a particle at liquid interface is important, then the particle disturbs the interface. However, if the particle is very small then gravity is negligible and does not induce any meniscus around itself. In cases where the particle is big, then gravity will induce meniscus around the particle. This argument is described with Bond Number ($B_0$) is,

$$B_0 = \frac{\rho_{\text{eff}} g d^2}{\gamma}$$

where $\rho_{\text{eff}}$ is effective density, $g$ is the gravitational acceleration, $d$ is the size of the particle and $\gamma$ is the interfacial tension.

Particles can be grouped in three depending on their buoyancies; heavy, neutral and buoyant. Heavy and buoyant particles cause the interface to deform in the downward and upward directions, respectively, while neutral ones do not cause any deformation. In the limit where the capillary length is infinite, the height of the liquid interface (height of the meniscus) around a particle satisfies $\nabla^2 h = 0$:

$$h(r) = h_0 \ln(r) + \sum_{n=1}^{\infty} h_n (1/r)^n \cos(n\varphi)$$

$h(r)$ describes the height of the meniscus around the sphere. In figure 5, a random contact line around the sphere is shown.
Figure 5: Random deformation of contact line around a sphere at a liquid interface.

The contact line around the sphere affects the capillary force on the sphere. The force on a small segment of the contact line can be described as $dF_{cap}$. Thus, total capillary force is:

1.12 $F_{cap} = \int \gamma dl \, \hat{t}(l)$,

where $\hat{t}$ is a unit vector that points tangent to the interface and perpendicular to the contact line. Particle interactions depend on the deformation of the meniscus as given above. Examples of heavy and buoyant particles are given in the figure below.
Figure 6: An example for heavy and buoyant spheres. On the left is a PDMS-coated glass sphere, on the right is a nylon sphere at water/air interface.

Particles that fall into the same category attract each other and opposite ones repel each other to minimize the surface energy of the liquid interface. Neutral ones are attracted by both heavy and buoyant particles\(^{(20)}\). The below schematic shows the cheerios effect\(^{(19)}\). The same type of particles attract each other while opposite ones repel each other in order to minimize the surface energy\(^{(19, 21)}\).
1.2. Particles at Liquid Interfaces

1.2.1 Contact Angle

The contact angle is one of the important parameters of wetting (22, 23). It is defined as the angle in between two rays, where one of the rays is parallel to the solid surface where it touches the contact line and the other ray is parallel to the meniscus (the fluid interface) at the contact line, as seen in figure 7. Each of these rays is perpendicular to the contact line as well as being tangential to one of the surfaces.
Figure 8: Contact angle of a liquid with a solid surface.

Figure 9: Sphere sitting at a liquid interface.

The contact angle of a sphere at the liquid interface is shown in figure 9. If the system reaches equilibrium, then the contact line should move to have a constant contact angle, given by the Young-Dupre equation. According to Young-Dupre Model, the contact angle can be found by using the force balance equation where the phases meet,

\[ \gamma_{SA} = \gamma_{SL} + \gamma_{LA} \cos \theta \]
where $\gamma_{SA}$, $\gamma_{SL}$ and $\gamma_{LA}$ are the surface tension between solid/air, solid/liquid and liquid/air respectively and shown in the figure below.

Figure 10: Liquid droplet on a solid substrate. Forces in Young-Dupre model is shown.

where, contact angle ($\theta$) is due to the balance of the surface tension of three phases.

As an example, a sphere at a planar interface would, in equilibrium, form a circular contact line with uniform angle in the absence of an applied force, and the interface would remain planar. If we put weight on this sphere, to satisfy the equilibrium constraint of constant contact angle and equilibrium of vertical forces the contact line around the sphere will move while maintaining the contact angle.

1.2.2 Contact Angle Hysteresis

In practice, the contact angle exhibits hysteresis (18, 24). The contact angle can have values in between advancing and receding angles which are definition for maximum and minimum values for a given surfaces (25).
Those angles can be found by; adding more liquid to the droplet will change the shape of the droplet and once the droplet reaches to it is maximum value of angle, the contact moves further (advances). This maximum angle, the drop has reached right before it moved is called advancing contact angle. (The droplet is expected to have this same angle as it moves, if it moves at negligible speed.) The reverse is correct for receding contact angle. When the liquid is sucked back from the drop, the angle will decrease until it reaches to a minimum angle before it moves backwards (recedes).

Advancing and receding contact angles can be static or dynamic advancing/receding contact angles. All the angles in this dissertation are static contact angles.

There are many models that explain the contact angle hysteresis, for instance, roughness of the surface (pinning), chemistry of the surface, prior wetting, and three-phase line tension (22, 26-36).

One of the most common things observed in wetting experiments is pinning. When a particle is adsorbed to a liquid interface, the contact line is not smooth if there is pinning at the macroscopic scale. When the three-phase contact is visibly
stuck at a point even when the particle is displaced, this can prevent energy minimization of the liquid surface. Thus, will cause contact angle to change. The contact angle of the liquid will increase/decrease until contact line can get over the barrier of pinning, in order for three-phase contact to move forward/backwards.

Contact angle hysteresis still raises many questions; it is not well understood yet in a general way and it is not yet possible to predict the advancing and receding angles for a given surface. Research on contact angle hysteresis has increased in the last 20 years due to its applications in technologies such as to make self-cleaning surfaces, self-drying surfaces, de-icing of surfaces (37-42).

1.2.3 Contact Line

If the shape of the contact line is specified and if the contact angle and mean interface curvatures are also specified, then the shape of the interface around a bound particle is known. Hence the deformation around the particle and the capillary force acting on it may be found from the contact-line shape. Those properties determine the boundary conditions of the particle at a liquid interface.

As said before, when a sphere is placed at a planar liquid interface, the contact line around the sphere is circular if the pinning is insignificant. If there is pinning, the contact line is unpredictable due to roughness or heterogeneity and does not make a perfectly circular shape around the sphere (43). The shape of the liquid interface affects the contact line around the sphere. If the liquid interface is anisotropic it deforms the contact line (it is not circular anymore) and the dipolar or quadrupolar component of the contact line becomes dominant (20, 44).
quadrupole, what is meant is that liquid rises along one principal direction and depresses along the other direction as seen in figure 12.

![Figure 12: Induced quadrupole around the sphere at cylindrical interface. Bird’s eye-view of the sphere. (+) & (-) refer to interface as rising and depressing.](image)

Positive sign and negative signs show the points the contact line rises and depresses. The direction of the quadrupolar deformation depends on the interface shape, as well as the contact angle (whether it is greater or smaller than 90°). The magnitude of the quadrupolar deformation around a spherical particle with zero net force is calculated to be (20, 44);

\[ z_2 = \frac{1}{6} D r_c^2 \]

where \( z_2 \) is the magnitude of the quadrupolar deformation, \( D \) is the deviatoric curvature and \( r_c \) is the contact radius of the sphere. This expression omits corrections that are smaller by a factor on the order of \((r_c D)^2\) (20).

The above description is true for a sphere. What about other shapes? The shape of the particle adsorbed to the interface is important for determining the
contact line shape. In order to satisfy constant contact angle boundary condition, meniscus around the particle would adopt to a different shape. Anisotropic particles such as, cylinders, cubes and ellipsoids at liquid interfaces are studied (7, 45-52). Unlike spheres at planar liquid interfaces contact line around those particles adopt different shapes and higher-order terms can be dominant.

Both contact angle and contact line are crucial for capillary interactions. Those properties determine the interaction of particles with each other at liquid interfaces. In this thesis contact angle and contact line around a spherical particles are studied at isotropic and anisotropic liquid interfaces in detail.

In this dissertation, the contact angle and contact line of spherical particles at planar and anisotropic liquid interfaces are studied. The flow goes as following: In chapter 2, the contact angle around a sphere (no pinning, PDMS-coated glass in millimeter-sized glass spheres) at planar and anisotropic interfaces is measured. The liquid interface is disturbed to a saddle or cylindrical shape to make it anisotropic. Apparent receding contact angles decreased from 101° to 80° degrees at anisotropic (cylindrical and saddle) interfaces compared to planar interface. In chapter 3, the time evolution of contact angle at smooth and rough surfaces is discussed. In chapter 4, the contact line around a sphere (no macroscopic pinning, contact line is smooth) at anisotropic interfaces and the contact line around solid particles of anisotropic shapes are studied. The contact line around the sphere at anisotropic interfaces deforms from circle. Quadrupolar deformation of the contact line is measured and compared to theory. A good agreement is observed among our results and the theory. Moreover, in chapter 4, some results are given for cylindrical
shapes. In chapter 5, long-range attraction short-range capillary repulsion between two spheres is described.
CHAPTER 2

EFFECT OF INTERFACE SHAPE ON CONTACT ANGLE

Contact angle is an important parameter for wetting and capillarity. According to the literature (and as summarized in Chapter 1), it is known that contact angle depends on the intrinsic properties of the surfaces such as roughness, chemistry and line tension (33-35, 53-57). In this chapter, the contact angle of PDMS-coated millimeter-sized glass spheres is studied at different shapes of liquid interfaces and interesting and new results have been found. At anisotropic liquid interfaces, we find that the apparent receding contact angle decreases. We define the anisotropy with deviatoric curvature $D_0$. As $D_0$ increases from 0 to 0.22 mm$^{-1}$, the receding contact angle decreases from 101° to 82°. To our knowledge those results are new to the literature and are likely to be important for future research on contact angle hysteresis and wetting.

In this part of the experiments, it is very important to get repeatable results of contact angle measurements and to get rid of pinning effect since it can directly affect the contact angle measurements. For the same reason, for those experiments controls are defined very well to observe the effect of the shape of the liquid interface only. For this purpose, glass spheres are coated with PDMS (polydimethylsiloxane). Sample preparation, procedure and controls of the experiment are described below in detail.

2.1 Experiment
2.1.1 Sample Preparation and Procedure to find contact angle

In the experiment, glass spheres that are 3.2 and 2.4 mm in diameter, manufactured by Winsted Precision Ball Company and purchased from McMaster-Carr (cat. no. 8996K21 & 8996K22) are used. First, for cleaning purposes, spheres are placed into sulfuric acid-nochromix mixture over night, then rinsed with DI water and soaked into DI water for 2 hours. These steps must be done with caution and the acid wash step must be done in a vented chemical hood because the acid is corrosive. Below, I describe ways in which this process may fail and what to look for.

Later, the washed spheres are dried in oven at 80° for another 2 hours. Once the spheres are dry, a thin rigid rod is attached on top of the spheres perpendicular to its surface. The rod is dipped into an epoxy (brand name: lactate, Part No: 83075). And then brought into contact with the sphere from top, perpendicular to its surface. In order for epoxy to cure, I waited approximately 2 hours. It is important to mix the epoxy well and wait long enough for epoxy to cure (after attaching to the sphere); otherwise, epoxy can melt at high temperature in the oven and affect the surface coating of the sphere. Then, spheres are dipped into the PDMS (polydimethylsiloxane, trimethylsiloxy terminated, 94 kDa; Gelest cat no. DMS-T22) and placed into the oven for 24 hours at 150 °C, following the directions given by Krumpfer et al (58). After 24 hours, the sample is taken out to cool down to room temperature. Once the sample reached the room temperature rod-attached sphere is taken from the PDMS bath and washed with toluene, acetone and DI water,
respectively. This way, the surface of the glass is coated with PDMS and the excess amount of PDMS is removed from the sphere by washing.

![Figure 13: Glass sphere at water/air interface, before (left) and after coating with PDMS (right). Pictures are taken through the air phase on the left side and water phase on the right side.](image)

As seen from the figure above, before coating the contact line around the sphere is highly pinned and undulated. This way, it is impossible to get repeatable contact angle measurements. One gets different results each time. However, after coating the sphere with PDMS, a smooth contact line is observed and repeatable contact angle measurements are made. This is the main purpose of coating the sphere with PDMS, to achieve a smooth contact line and repeatable measurements of contact angle. However, sometimes coating might not work.

![Figure 14: Example of sphere, where PDMS-coating did not work. In such a case, those spheres are not used.](image)

In figure 14, an example of two spheres, which did not pass the control experiments, are given. The reasons for unsuccessful coating rely on cleaning
process of the spheres. If they are not cleaned well, then coating is not homogeneous and there are big jumps in the contact line.

I have worked out step by step to find out reasons why PDMS-coating does not work and yields an undulated contact line sometimes. One of the most important reason for the coating not to work is that if the sphere does not get cleaned very well in the acid-wash step and if one does not wait long enough for epoxy to cure might cause big undulations in contact line as well. Since glass is hydrophilic, if one part of the sphere does not get coated it creates big undulations as seen on figure 14. When the sulfuric acid used has been exposed to humidity for too long it does not matter how much Nochromix is added: the washing process is not successful. The potency of the acid mixtures can be tested by placing a drop on a piece of paper. If the Nochromix/sulfuric acid works, it burns the paper very fast. My tests show that when the sulfuric acid is mixed with Nochromix and waited long time, it does not pass the paper test and does not clean the glass spheres and the coating does not work homogeneously. In short, the time of sulfuric acid exposed to Nochromix is important. Thus, I keep the bottle of sulfuric acid exposed to Nochromix separate from the unused stock bottle of acid. Each time I mixed fresh sulfuric acid with the Nochromix. These steps are important, though tedious to go through very carefully.

Once the sphere passes the control experiments, which will be described shortly, it can be used to test the effect of interface shape on contact angle. Before starting each experiment we wash rod-attached spheres with DI water and dry them with pressurized air. Moreover, since spheres are coated with PDMS, we do our
measurements using freshly coated spheres (we suggest to use them within 7 days after coating). And finally, we mount our rod-attached sphere on a stage to be able to move it up and down through the interface (Figure 15).

![Diagram](Image)

**Figure 15: Schematic of the experiment.**

As we move the stage down, the sphere gets pushed into the water. In this process water is advancing across the sphere surface. However, in the reverse direction water recedes. Thus, we push our sphere into the interface slowly and stop to take pictures. Contact angle through pushing in and pulling out process is shown in figure 16. Contact angles are plotted with respect to depth. Depth here means simply how much the sphere is pushed into the water such as zero depth ($L_0$) is where the sphere meets with water for the first time. In this example (Figure 16), the sphere is pushed in with an amount depending on the diameter of the sphere and then pulled back up tracing the same path. As seen from the figure consistently contact angle in the pushing down process is equal in each depth and in both sides of the sphere. This angle is called apparent advancing angle, since water is
advancing through surface of the sphere as pushed into the interface. On the other hand, as the sphere is pulled back up, water recedes through the sphere surface, this angle is called apparent receding angle.

While changing direction from advancing to receding, some angles, which are neither advancing nor receding are observed. Those angles are called transient angles (59). If you were to draw a line following advancing to receding and back to advancing you would get a trapezoid shape called hysteresis loop (60) (Figure 16). This was one of the control experiments done. Black and pink colors correspond to data points that are done following each other without losing the contact with the interface. And finally, blue data points are taken after the sphere is tested at anisotropic interface. All data points agree with each other. Thus, one can conclude that for a given sphere (r=1.6mm), apparent advancing angle is 109 ± 1° and apparent receding angle is 100 ± 1°. The contact angles at the left and right sides of the sphere are shown in figure 16. When I take the sphere out and rotate about the axis of the rod, and then place back into interface shows indistinguishable advancing and receding contact angles. So, the angle is independent of orientation of the sphere as one might expect. Moreover, with our method of measurements, we can only measure the contact angles from two points, left and right sides. However, we observe the contact line is smooth and circular. This shows that at planar liquid interface contact angle around the PDMS-coated sphere is constant.
Figure 16: Hysteresis loop of contact angle. Filled and empty shapes are for left and right sides. Black and pink data taken following each other without losing the contact with the interface. Blue data is taken after doing the experiment at saddle shape. The secondary sphere is removed and hysteresis loop of target sphere is measured.

This figure shows the hysteresis loop of our sphere as it is pushed into the interface and pulled out. Apparent advancing and receding angles are measured $109 \pm 1^\circ$ and $101 \pm 1^\circ$, respectively. Errors are estimated from 3 repeated measurements of the same image and by repeating the measurements after changing the illumination 5 times.

As seen in the figure 16, at around $L_D=1$-$2$mm depth, no data is taken because of the fact that height of the contact line around the sphere is at similar level as the
planar liquid interface further away from the sphere. Thus, we cannot see the contact line around the sphere and cannot make measure the contact angle. As described before, from \( L_D = 3.7\text{mm} \) to 3.3mm recorded angles are transient angles. (This number can change depending on the size of the sphere, given example is for a sphere radius =1.6mm)

Another control experiment is the time evolution of the contact angle. Since all the measurements are done at static case it is necessary to know how long it takes for contact angle to find its equilibrium value. Contact angle of PDMS-coated glass sphere is time independent. Even the transient contact angles are very stable. They do not change in time. As the sphere is moved from one height to another, contact angle changes instantly. More information on time evolution of the contact angle is given in chapter 3.

Those steps are necessary controls before starting the experiments at anisotropic interfaces. If a sphere does not pass the control at some point that sphere is not used for the rest of the experiments.

2.1.2 Contact Angle Measurements

In order to find the contact angles, we used two methods called as geometric and analytic methods. In geometric method, ImageJ image analysis software tools are used to find the contact angle. First, we fit the glass sphere to a circle and draw a line tangent to the sphere where it meets with the interface and another line parallel to the meniscus. Contact angle is the angle between these two lines.

To find the contact angle analytically, we fit the tangent line and interface close to sphere to a line function. The meniscus or deformation around a single
('target') sphere, placed in an initially flat interfaces, decays as $z(y) = A \ln(y-y_T)$ if $(y-y_T) << L_c$, where $y_T$ is the center of the target sphere and $L_c$ is the capillary length $(\gamma/gp)^{1/2}$. For a water-air interface, $L_c = 2.7$ mm. We use coordinates where the interface height is $z$, the sphere is centered at the origin, and the camera images the $y$-$z$ plane. If there is another, secondary, sphere (two-sphere case will be described later) at position $y_S$ close to the target sphere, then the interface at the target sphere is no longer isotropic in shape and one expects an induced quadrupolar deformation around the target sphere, proportional to $1/(y-y_T)^2$.

To fit the right-hand side of the target sphere (the side that is far from the secondary sphere), we fit the interface height to this function:

$$2.1 \quad z(y) = A \ln(y-y_T) + B \ln(y-y_S) + C/(y-y_T)^2 + E,$$

where $A$, $B$, $C$, and $E$ are fit parameters. The first and second terms describe deformations surrounding each sphere and the third term describes the induced quadrupolar deformation around the target sphere because of the secondary sphere. We obtain good fits to this function within a distance of 2.7 mm.

To fit the left side of the target sphere (which is close to the secondary sphere), we must add an extra term to account for the fact that the target sphere induces a quadrupolar deformation about the secondary sphere. (This term becomes quite small on the far side of the target sphere so it was not included in the right-hand-side fit.) We fit the left section of the interface to the following function:

$$2.2 \quad z(y) = A \ln(y-y_T) + B \ln(y-y_S) + C/(y-y_T)^2 + F/(y-y_S)^2 + E,$$
and the values of the fit parameters \((A, B, C, E, F)\) may be different from the right-hand side. The fourth term is added to account for the fact that the target sphere can also induce quadrupole around the secondary sphere.

![Image of a single sphere receding at a planar liquid interface.](image)

Figure 17: Single sphere receding at planar liquid interface. \(a=1.6\text{mm}\).

For an example, following plots show the fits to meniscus on the left and right sides of the sphere. Figure 18 and 20 show the fits to the meniscus around the target sphere in figures 17 and 19.
Figure 18: Pixel coordinates of the meniscus on the left and right sides of the sphere.

From figure 18, we measure receding contact angle to be 102.6 and 102.2 on the left and right sides of the sphere. This data is shown in figure 21, red data point at $D_0=0$. Receding contact angle measured from figure 20 is 91°.

Figure 19: PDMS-coated sphere at saddle-shape interface. Target sphere is on the right side. Spheres' size are the same, $a=1.6$mm.
From the fitted shape of the interface, we extracted the tilt angle of the interface at the contact point. We then found the tilt angle of the sphere’s surface at the contact point by superimposing a circle on the image of the sphere and finding the tangent at the contact. The contact angle, $\theta$, was then calculated from these two angles (red data in Fig. 21).
As seen in figure 21, measurements from both methods agree with each other nicely. This fitting method removes much of the opportunity for measurement bias and also gives a measurement that is independent of the geometric method. Fitting also allows us to verify that the interface shape is as expected and indicates the lack of contaminants or defects that perturb the interface shape (which is also checked directly).

2.1.3 Preparing Anisotropic Liquid Interfaces

In this dissertation, saddle-like and cylindrical like interfaces are used in order to find the effect of the interface shape on contact angle.
In order to make a saddle like liquid interface a secondary sphere, which could be hydrophilic or hydrophobic, is used. In order to make the secondary sphere hydrophilic it is washed with Potassium Hydroxide (KOH, from Mallinckrodt AR ACS, Lot No: 6984'T21H07) following the NoChromix/sulfuric acid wash. KOH pellets are placed into ethanol at a concentration of 15 weight %. In order to dissolve the pellet in the ethanol, magnetic stirrer is used. The cap of the container is closed with aluminum foil in order to prevent evaporation. When the whole KOH pellets are dissolved in the ethanol, the rod-attached clean (nochromix sulfuric acid washed previously) is dipped into the solution and sonicated for 5 minutes. Later, the rod-attached sphere is washed with DI water many times and sonicated with DI water for 5 minutes. Lastly, it is washed with ethanol and placed into oven at 60 °C for 1 hour. When a glass sphere is washed with KOH+ethanol solution its surface is very smooth and no-pinning is observed. KOH washed glass sphere has a very small
receding angle measured to be around 15°. When the secondary sphere is dipped into the interface and pulled back up (still keeping its contact with the interface), since it has a very small receding angle it causes a high deformation of interface around itself and since it has a smooth contact line, the disturbance of the interface around the secondary sphere is symmetric (Figure 22a).

On the other hand, to change the direction of saddle interface instead of a KOH glass sphere secondary glass sphere is coated with PDMS and pushed into the water in (Figure 23c). Both PDMS-coated and KOH washed sphere show no-pinning properties. This way, the interface shape has reflection symmetry about the vertical plane that contains their centers of mass.

Once the secondary sphere is placed into the liquid interface, as described above, the target sphere is brought to the interface. Centers of the spheres are kept in plane perpendicular to the axis of camera (Figure 23a, 23c). Secondary spheres used in those experiments are of the same size as the target spheres. By changing the separation of the spheres, anisotropy in the interface shape can be controlled. Moving the target sphere closer to the secondary sphere increases anisotropy. However, at the very short separation limit, bridging might play a role. It is important to avoid the bridging affect by observing the direction of the liquid movement. What bridging affect means is that, as the target sphere is pulled up, instead of interface to recede, it might move upwards with the sphere. Then, the angle measured is not a receding angle. I return to this point below.
Figure 23: Target sphere (on the right side) at the saddle (a, c) and cylindrical (b) shaped interfaces.

On the other hand, in order to make cylindrical liquid interfaces either two glass slides or two razor blades are used. Two glass slides are placed parallel to each other to make the interface cylindrical. Glass slides were washed either with KOH+ethanol solution to make them hydrophilic, or coated with silane to make them hydrophobic. The KOH washing process was done in the same way as explained above for glass spheres. For silanization, glass slides are washed in sulfuric acid/Nochromix mixture over night. Later washed with DI water for 2 hours and dried in the oven for 2 hours. Later, in one container 2ml of dichlorodimethylsilane is mixed with 100ml of toluene. The clean and dry glass slide is dipped in and left for about 3 minutes. Afterwards, glass slide is washed with ethanol, water and methanol, respectively. Then, glass slides are glued to parallel to each other about 3-5 mm apart depending on how much curvature of the interface is desired.
Alternatively, two razor blades are used, placed in a way that tip of the razors face each other and the container is filled with water, it would make a cylinder like shape (Figure 22c). In those cases, along one of the principle curvature directions length of the cylinder is much bigger than the size of the sphere. Thus, that side has zero principal curvature. Changing the separation between the glass-slides or razor blades can control the magnitude of the other principal curvature. In order to quantify the anisotropy of the liquid interface, deviatoric curvature ($D_0$) is used. In order to find the $D_0$, geometric properties of spherical cap is used (As seen in Fig. 22c it looks like a spherical cap). One can find the radius of the circle by using this relation,

$$R = \frac{m^2 - h^2}{2h},$$

where $m$ and $h$ are the radius and height of the cap, and $R$ is the radius of the circle. The figure below shows that the interface fits to a circle.

![Figure 24: Circular fit to the interface in between two razor-blades.](image-url)
As seen from the figure above, our data nicely fits to a circle. The radius of the circle is found as 3328px, whereas with geometric argument I found 3501px. The difference is about 5%. For simplicity, for the rest of the data geometric argument is used to find the radius of the cap.

2.2 Anisotropy of the Interface/Deviatoric Curvature

Anisotropy of the liquid interface is defined by deviatoric curvature \(D_0\), which is the difference between the principle curvatures;

\[
D_0 = \frac{c_1-c_2}{2},
\]

For instance, in order to find \(D_0\) of a cylindrical interface one needs the principal curvatures, as showed in the Fig. 25;

![Figure 25: Cylindrical liquid interface.](image)

According to the definition of \(D_0\), planar and spherical liquid interfaces have zero deviatoric curvature and others such as saddle and cylindrical liquid interfaces would have a non-zero deviatoric curvature.

In order to calculate the deviatoric curvature of the liquid interface different steps are followed depending on the shape of the interface. If it has a saddle like
shape, as shown in Figure 22, one can take the pixel coordinates of the interface on the left side of the secondary sphere.

![Figure 26: Schematic of saddle interface.](image)

And this line is fit to following function:

\[ z(y) = A \ln(y-y_T) + B \ln(y-y_S) + C/(y-y_S)^2 + G \]

\[ c_1 = \frac{y''}{(1+y'^2)^{2/3}} \]

and from this fit, one of the principal curvatures, \( c_1 \), is found by using equation the above equation, at where the center of the target sphere would be. Once \( c_1 \) is found, one can easily find \( c_2 \) by using the fact that

\[ H = \rho g h = \frac{c_1-c_2}{2}, \]

where \( h \) is the height of the liquid interface where the center of the sphere would sit, measured from the height of the planar liquid interface. Error that can be made with method is found to be about 0.006 mm\(^{-1}\) and comes mostly from the measurement of height of the center of the sphere from the undisturbed interface.
2.3 Results

Contact angles of the same sphere are compared at different liquid interfaces. In these kinds of experiments, it is important to be precise. However, contact angles can adopt a range of values: how can one compare those numbers? In order to avoid this, I have compared apparent advancing and receding contact angles. It is always made sure that interface is fully advancing or receding through the surface. In fact that is one of the reasons for using PDMS-coated spheres. They do not create pinning (in macro level). Still, there are some transient angles when changing direction from advancing to receding (Figure 16), which could be avoided by letting the interface to recede or advance fully. In practice, transient angles are observed while transferring from advancing to receding only. In some experiments, I observed transient angles while changing direction from receding to advancing. However, those measurements were not repeatable.

Measured angles in this dissertation are static contact angles only. Measurements are done, after the motion of the sphere/cylinder has stopped. In this case, one might wonder about the time evolution of the contact angle. Contact angle of the PDMS-coated sphere is time independent. This subject will be described in detail in chapter 3.

Static apparent advancing and receding angles have been observed at many different liquid interfaces. Repeatedly, apparent receding angle has shown differences compared to a planar liquid interface(61). In the following plot receding angles of PDMS-coated spheres with radius $a = 1.2$ and $1.6\text{mm}$ are shown at saddle and cylindrical liquid interfaces.
Figure 27: Receding contact angles at saddle and cylindrical interfaces.

In this plot, receding angles of spheres which initially (at planar liquid interface, $D_0=0$) had $\theta=100^\circ$. In figure 27, square and star shapes correspond to positive and negative deviatoric curvature according to my definition of principle curvatures. Moreover, filled and empty shapes correspond to receding angles at left and right sides of the spheres.

As seen from figure 27, contact angles are indistinguishable but what about the other directions? These measurements are done at the plane perpendicular to the camera axis. For instance, at around $aD_0=0.06$ star and square shapes show almost the same receding angle. Although measurements are done at different liquid
interfaces, this tells us that for a given $aD_0$, receding contact angle is the same at 4 maximum and minimum points. Relating those results I conclude that contact angle around the sphere is constant. However, as just mentioned contact angle measurement are only done at 4 points around a sphere at cylindrical interfaces. Experiments with Wei He, a fellow graduate student in the UMass Physics Department in Prof. Dinsmore’s Lab, with a sphere of $a=1.2\text{mm}$ at a cylindrical liquid interfaces, $D=0.13\text{mm}^{-1}$ is measured the same at the 2 perpendicular directions (Fig. 28).

![End view](image1.png) ![Side view](image2.png)

Figure 28: Instant pictures of PDMS-coated sphere on a cylindrical interface. Images are taken from end-view and side-view. The sphere size in this picture is $a=1.2\text{mm}$. Deviatoric curvature of the interface $D_0=0.13\text{mm}^{-1}$.

Initially, this sphere had receding contact angle of $93^\circ$, however, at cylindrical interfaces it’s receding angles were measured, with two camera places perpendicular to each other, as $80^\circ$.

In our experiments, some PDMS-coated glass spheres had values different than $100^\circ$. The following plot shows all the data.
Figure 29: General plot of $\theta_r$ vs. $aD_0$. Each shape has different receding contact angles at planar interface ($aD_0=0$). Sphere sizes are $a=1.6\text{mm}$ and $1.2\text{mm}$ for filled and empty shapes, respectively.

In this plot, different shapes show different $\theta_r$ at $aD_0=0$. Experiments with those spheres at $D_0 \neq 0$, show different receding angles. Our results show that $D_0$ systematically causes a change in contact angle. Thus, difference in cosine of the contact angle is the important parameter. As seen in the plot, $D_0$ causes the $\theta_r$ to change some amount. This change is independent of the initial contact angle for the angles studied here.
Figure 30: Difference in cosines of receding contact angle at curved and planar interfaces vs. $aD_0$.
Sphere sizes are $a=1.6\text{mm}$ and $1.2\text{mm}$ for filled and empty shapes, respectively.

where $\theta_p$ and $\theta_c$ are the receding contact angles at planar and curved interfaces, respectively. It is not very clear whether the difference in cosine of the angles (Fig. 30) or cosine of the difference in angles (Fig. 31) is the important parameter.
Figure 31: Cosine of difference in receding contact angles between planar ($\theta_P$) and curved ($\theta_C$) interfaces vs. $aD_0$. Sphere size is $a=1.6$mm and $1.2$mm for filled and empty shapes, respectively.

On the other hand, no difference is measured in apparent advancing angle around the sphere. All the advancing angles measured in all those experiments were $108\pm2^\circ$. Our results show strong dependence of apparent receding angle on shape of the liquid interface while advancing angle does not depend on the shape.

### 2.4 Discussion

In my experiments, I have shown that the receding contact angle decreases systematically as the liquid interface gets anisotropic ($D_0$ increases)(61). On the other hand, no difference is observed in advancing angle. So, what causes the receding angle to change but not the advancing angle? We have worked on many possible reasons that might be the reason for receding angle to change. Contact angle has been known as property of material and interfacial tensions. However, repeatedly we have shown that shape of the liquid interface affects the contact
angle. We believe that contact angle has to be a local property that is obviously affected by the shape of the liquid interface.

One of the possible explanations of the contact angle to change might be the one-dimensional line tension (energy per length of the 3-phase contact line). If we consider contact angle to change due to line tension as proposed by Tadmor et al\cite{34, 35, 62, 63}, this would cause change in angle depending on where the contact line is. For instance, if the contact line were above/below the equator of the sphere the line tension would cause the contact angle to be bigger/smaller. This contradicts our results. Thus, 3-D line tension effect on contact angle does not explain our results.

The contact line around the sphere is circular when it is placed at a planar interface, however, when the interface shape gets anisotropic contact line changes its shape as well. The contact line gets longer and goes out of plane. When the sphere is pulled up contact line sweeps on the sphere. This requires some energy per area when the wet surface goes to non-wet (dry) state. Thus, there might be non-reversible energy that needs to be paid in order to go from wet-to dry state. This extra energy might be paid by the angle around the sphere. This might explain the decrease in receding contact angle at curved interfaces. However, Dr. Vincent Demery, our collaborator, showed that this is independent of the shape of the liquid interface.

Our ideas did not explain our results. However, our results are repeatable, solid, and observed for different spheres and different interfaces. We agree with the current idea of contact angle being a local property of 3-D contact of phases. Thus, it
is very probable that receding contact angle is changing due to the contact line deformation at curved liquid interface. The shape of the liquid interface might be considered an external parameter that causes a local deformation (deformation of contact line). For this purpose and other purposes contact line around a sphere and other shapes is studied and more information can be found in chapter 4.
CHAPTER 3

TIME EVOLUTION OF THE CONTACT ANGLE

3.1 Introduction

Time evolution of the contact angle has been one of the questions that surface scientist has worked on for years. Contact angle, grouped as static and dynamic, is a complex phenomenon to understand and measure (23). Dynamics of contact angle is important as well as the equilibrium contact angle (9). Much research has been devoted to understand the dynamics of wetting at solid surfaces (64, 65).

The interest of this chapter is on dynamics of contact angle of adsorbed particles at liquid interfaces. It is always said that when a particle adsorbs to an interface, it finds its equilibrium position. Experiments done by Kaz et. al show that for micrometer-sized spheres the contact angle evolves logarithmically with time and it may take so long to come to an equilibrium (66). Effects of roughness and heterogeneity of the solid surface on dynamics of contact angle have been studied (22, 67). However, these questions have not been answered yet: how long does this process take? What physical properties does the rate depend on, such as heterogeneity of the surface, scale of roughness? Does gravity have an effect on it? Thus, what is the time evolution different for different scales of particles? Does it depend on shape of the particle? The time evolution of the contact angle, including the question of whether the angle always tends toward the Young-Dupre values, is another important open question in the literature.
To introduce our perspective on this area: we study the time evolution of the advancing and receding angles separately, since dynamics of those two angles are not necessarily the same. We also study the effect of roughness (pinning scale) on millimeter-sized spheres, where gravity is not negligible. Our work raises new questions in this area, which will be given at the end of this chapter.

3.2 Experiments

Pinning is an important parameter for dynamics of contact angle. When the 3-phase contact is pinned at some point, it might take a long time to get rid of that energy barrier due to pinning. We first studied the time evolution of spheres with macroscopically smooth and rough surfaces. For smooth surfaces, PDMS-coated glass spheres, with a radius $a = 1.6$ mm, are used. Those spheres were attached to a rigid rod in order to make it easy to handle as in experiments in chapter 2. The sphere is pushed into the air/water interface and advancing contact angles on the left and right sides are measured. In order to measure the receding contact angle, the sphere is first pushed all the way into the water and then pulled all the way back up from the interface, and angles from left and right sides are measured.
Figure 32: Time evolution of advancing and receding angle through macroscopically smooth surface. It is a PDMS-coated glass surface.

The above figure shows the advancing and receding angles of left and right sides of a PDMS-coated glass sphere at the water/air liquid interface in the first 5 minutes. The contact angles reach a steady value in a time shorter than we can measure. This has a practical use; as the sphere is moved through the interface one wonders how long to wait before making the measurements, and how the delay time might affect the experimental results (43, 68, 69). For a good control, one should know the time evolution of their particles at liquid interfaces. Since these spheres almost instantly go to the steady-state point, after each movement (in either direction, advancing or receding) we counted to 5 seconds before making the measurements.
Measurements are done up to 5 minutes only at air/water interface. There are two reasons for this. Firstly, we would like to see how consistent our contact angle measurements are when made 5 s after the sphere is moved. Since the contact angles do not change within the first 5 minutes we do not need to check for longer times. Secondly, those experiments are done at air/water interfaces, where there is an effect due to evaporation. At the room temperature, evaporation effect is irrelevant in the first 5 minutes as seen from the figure 32. Evaporation can affect the values for advancing angle because the contact may recede if enough water evaporates. This is not a problem for the receding angle.

Coating the sphere with PDMS makes its surface macroscopically smooth. Images at both advancing and receding cases show circular and constant contact line around the sphere. In figure 33, AFM image of a PDMS-coated glass surface is given.

![AFM image of PDMS-coated glass sphere. Sphere size 3.2mm. Label name=M3.](image)
Figure 34: Height profile of the PDMS-coated glass sphere surface.

Figure 34 shows AFM measurements of surface height profiles of a PDMS-coated sphere. The root-mean-square height is 13 nm.

The time evolution of macroscopically smooth and non-smooth (rather rough) surfaces, are compared. For the latter, acrylic spheres with radius \( a = 1.59 \) mm, are used. They were purchased from McMasterCarr.com (cat number: 1383K42), washed with soap and soaked into DI water for at least 30 minutes to remove the soap from the surface totally. Figure 35 shows time evolution of an acrylic sphere, attached to a rigid rod and pushed in to measure the advancing contact angle and pulled back up to measure the receding contact angle.

Figure 35: Time evolution of advancing and receding contact angles of non-coated acrylic sphere (\( a=1.6\) mm) at water/air interface.
The dynamics of the advancing and receding contact angles of acrylic is given in figure 35. PDMS-coated surfaces, compared to acrylic, find a steady value in a measurable time. This difference might be due to surface roughness or heterogeneity. The right way to test the effect of roughness would be to focus on surfaces with the same chemistry (heterogeneity) but different roughness scales. This is one of the points proposed for future experiments, later in this chapter.

When a free, rough sphere is placed into the liquid interface, how does the contact angle change? Previous experiments in this chapter show time evolution of spheres at a given height. We now turn to measurements with a free sphere placed to a liquid/liquid interface. Since a sphere is free to move along the interface, it was not accurate to measure the contact angles from left and right sides with the camera we used (Panasonic GP-KR222) because of the quality of the images. The focus on meniscus where it meets with the sphere surface was not very clear. Thus, time evolution of the contact-line diameter was measured instead.

A free acrylic sphere with a diameter of 3.2 mm is placed into the interface between an aqueous solution of sodium polytungstate (from Aldrich, part no: BCBG4815V, 40% weight percent added to raise the mass density of the solution to 1.45 $\text{kg/m}^3$) and silicone oil (from Sigma-Aldrich, Lot no: MKBR6904V, $d=1.05 \text{ g/mL}$). As the sphere sinks into the interface, the apparent diameter of the contact line at the solution/silicone oil is measured. Because the silicone oil is not volatile, there is no observable evaporation during this experiment.
Figure 36: Time evolution of contact line. Each color corresponds to different acrylic sphere with the same size (a=1.6mm). Planar Polytungstate/silicone oil interface.

Different colors correspond to different trials with different spheres. Figure 36 shows that there is a big change in the first 200 minutes and then the change in contact diameter slows down for most of the data points. Our rough sphere results agree qualitatively with the results of Kaz et. al (66) with micro-sized spheres. Unlike their experiments, we used millimeter-sized spheres, where gravity played a big role.

Long-term experiments are repeated at water/silicone oil interface with the acrylic spheres with the same radius (1.6mm). Again, the acrylic sphere is allowed to float freely at the interface. Trend of these experiments is similar with the previous interface. Slopes of the two plots are indistinguishable. However, the
magnitude of the contact diameters is different, as expected because these experiments were done without polytungstate. Therefore the spheres had a downward force owing to gravity and the contact diameter was consistently larger (Figure 37).

![Graph showing time evolution of contact radius of an acrylic sphere at a planar polytungstate/silicone oil interface (Figure 36) vs. DI water/silicone oil interface (light green star shapes)].

Figure 37: Comparison of time evolution of contact radius of an acrylic sphere at a planar polytungstate/silicone oil interface (Figure 36) vs. DI water/silicone oil interface (light green star shapes).

The figure above compares the values when instead of polytungstate solution just DI water is used. One of the questions to answer is that how does free charges play a role in binding on colloids at the interface. Given experiments are not complete and not enough to make conclusions out of them. In the next section, I propose well-defined experiments to answer those questions.
I have also studied time evolution of polystyrene (PS) spheres (purchased from McMasterCarr.com, a=1.6mm). In the figure below, PS sphere is at water/silicone oil interface.

![Figure 38](image)

*Figure 38: PS released to water/silicone oil interface. Left image is taken 2 minutes after it is released. Right image is taken 70 minutes after the release.*

Figure 34 shows time evolution of contact diameter of a polystyrene sphere with a radius of 1.6mm. First and second images are taken 2 and 70 minutes after the release. In this time, contact diameter has increased from 0.95 to 1.25mm.

![Figure 39](image)

*Figure 39: Time evolution of PS at water/silicone oil interface. First 70 minutes.*
In those examples, time evolution of contact diameter of acrylic, polystyrene spheres are given. Those spheres were freely placed to the liquid interfaces and contact diameter measurements were done. We have not measured contact angle since the quality of those images were not good, it is hard to nicely focus on the point where the interface meets with the sphere since the spheres are free to move around. Blurry images and reflection of light from the interface make it hard to focus.

3.3 Future Experiments

Our results show that there are many interesting open questions about the time-evolution of contact angles and contact-line shape. For future experiments, I suggest comparing the above values with receding cases. This would be done by starting the experiment from the lower liquid, and let the sphere reach the interface from below. Time evolution of contact angle is not necessarily the same in both cases. We can consider the motion from above liquid through the interface as advancing and motion from lower liquid to the interface as receding case. So, in those cases, does the contact angle reach to Young-Dupre Angle over time? Or do they reach to steady advancing and receding contact angles? How would roughness play a role in time evolution of contact angle and contact line? How does forces play a role in the time evolution. The force due to capillarity is related with the contact line and contact angle. Is the shape of the contact line predictable or not? How does the multipole expansion of the contact line \( z_n = \cos(n\varphi) \) change over time, and do different orders decay at different rates?
In summary, we have compared the time evolution of advancing and receding angles separately for macroscopically smooth and rough spheres. Contact angles are time independent at smooth PDMS-coated glass spheres. However, at rough surfaces (acrylic, nylon and polystyrene), the time evolution of the contact angle is very slow; the contact diameter increases logarithmically in time for a period of 3000 minutes, repeatedly. We still do not know if the contact angle ever goes to equilibrium (66). It is an open question.
CHAPTER 4

SPHERES AND ANISOTROPIC PARTICLES AT ANISOTROPIC
INTERFACES

4.1 Introduction

In this chapter, the effect of interface shape on meniscus around a spherical
particle and a cylindrical particle is studied. We focus first on spherical particles at
planar and cylindrical interfaces, and then we turn to cylindrical rods at planar
interfaces. We measured the shape of the contact line and performed a multipole
expansion so that we could measure the monopole, dipole, quadrupole and higher-
order contributions. To our knowledge, this is the first time that the contact line
deformation around a sphere was observed and measured directly. With those
direct observations we measured the magnitude of the quadrupolar deformations
around spheres that were induced by anisotropy of the interface shape. For the
advancing contact line experiments, we find agreement with theory. For receding
contacts, however, we find a larger quadrupolar deformation than predicted. We
also find that the deformation amplitude depends on the vertical force on the
particle, which was not anticipated. Previous experiments showed that there is
square-symmetry packing of spherical particles on saddle-shaped interfaces, which
qualitatively shows a quadrupolar deformation(70). Our results are the first to
quantify the quadrupolar deformation. We then turn to measurements of the
contact angle around a cylindrical particle oriented at a controlled angle relative to
an initially planar interface. Again we look separately at advancing and receding
contacts and we find that the contact angles are not uniform and they depend on the angle of tilt of the cylinder.

The remaining sections of this chapter describe electrostatic analogy in section 4.1.1, contact line analysis in section 4.2 and contact angle measurements of cylinder at planar interface in section 4.3. All of the results have been summarized in section 4.4

4.1.1. Background: the electrostatic analogy and the effect of geometry on the contact line

For simplicity, analogy to electrostatics is made to define the shape of the meniscus around the particles. The analogy is between the height of the interface in the capillary problem ($u(x,y)$ is defined as the height at every point above a reference surface) and the electric potential $\phi(x,y,z)$. For the special case where $\nabla u << 1$, the mean curvature of the interface is $\frac{1}{2} \nabla^2 u$. In the absence of external forces, $\nabla^2 u$ is constant, which resembles Poisson’s equation of electrostatics for the special case of uniform charge density in two dimensions. The height field can be defined by monopole, dipole, quadrupole and higher terms (71). Thus, first term of the equation from equation 4.3 is the monopole ($n=0$), $n=1$ and 2 correspond to dipole and quadrupole terms, respectively. If the particle at a planar interface were a sphere with no pinning, it would deform the meniscus symmetrically around itself, which corresponds to a monopole. The dipolar term appears when the contact line is tilted. The next term in the multipole expansion of the deformation is quadrupolar (43). This term is defined by;
$z = z_2 \cos (2\phi)$,

where $z$ is the height of the meniscus at the contact line, $z_2$ is the magnitude of the quadrupolar deformation, and $\cos(2\phi)$ is the symmetry of the deformation around the sphere (from Eq. 4.3, below). When there is a quadrupolar deformation, the meniscus around the sphere rises along one direction and depresses along the perpendicular direction.

The shape of the liquid interface affects the meniscus shape around the particle. It was first predicted by Wurger that, a sphere at curved (catenoid shaped) interfaces induces quadrupolar deformation around itself (44). This work has been extended by Zeng et. al(20), where the deformation of the contact line around a sphere at cylindrical interface was studied and the results used to obtain a conjecture for the general form of the leading-order shape deformation. These authors concluded that the Gaussian curvature $G$ should determine the quadrupolar deformation around a sphere, proportional to $G$. Ershov et al. (70) then suggested that the deviatoric curvature $D$ (defined in Chapter 1) should instead be the relevant parameter describing the interface shape.

Particles with anisotropic shapes can induce quadrupolar deformation as well, even at a planar interface. Meniscus around the anisotropic particles (cylinders, ellipsoid) rises along one direction and depresses along the other, depending on the contact angle of the particle. However, for non-smooth shapes like a cylinder, the meniscus is more complicated near the corners. The meniscus around these shapes changes sign in order to obey the constant contact angle boundary condition. However, it is still an open question, if the contact angle around
anisotropically shaped particles, is constant. Loudet et. al have shown that an ellipsoidal particle’s average contact angle decreases with the aspect ratio of the ellipsoids (49) and have a non-uniform contact angle. This latter observation is attributed to the method by which the particles were made: a common way of making ellipsoid is to stretch them (72), which might cause the surface of the particle to be heterogeneous, thus, causing to have different contact angle.

4.2 Spheres at Anisotropic Liquid Interfaces

4.2.1. Preparation of the Experiment:

In this part of the experiment, glass spheres, diameter of 3.2 mm, purchased from Mcmastercarr.com (cat. No; 8996K22) are used. The spheres are cleaned, coated with PDMS and attached to a rigid rod. Details of this procedure are given in chapter 2. For this part cylindrical interfaces are used. Cylindrical interface (Fig. 41b) is forced by placing two razor blades facing each other (explained in chapter 2). Once the sphere and interface are ready the experiment is started, explained in the next section.

4.2.2 Procedure

Typical experiment starts at planar liquid interface for control experiments. It is first checked, if the sphere surface is ready for the experiment. In order to test this, advancing and receding contact angle measurements are done at planar liquid interfaces. The sphere is pushed into the interface and then pulled back out. Control experiments are described in chapter 2, in detail.
Once, the sphere passes the control experiments at planar liquid interface, the sphere is then tested at the cylindrical interface. One can separate the experiment into two parts, advancing and receding. In the first part, the sphere is pushed into the interface. Usually after pushing the sphere about 1 mm into the interface, contact line around the sphere is observed through the water phase. Before that, the contact line is not observable since it is at the same level (height) with the undisturbed interface due to the contact angle constraint (\( \theta \approx 90^\circ \)). Once, the contact line is at observable region (when contact line is below the undisturbed interface), the sphere is pushed in some small amount (0.2 mm) and stopped each time to take a picture and moved down again and another picture is taken. Thus, all the measurements are done for static case. After each increment, waited about 5 seconds for contact line to cease. As shown in chapter 3, time evolution of the contact angle of PDMS-coated glass sphere is immediate. Thus, 5 seconds is long enough for contact line to be stable.

In the second part, the receding part, the reverse process is done. The experiment starts with a sphere, fully immersed into the interface. The sphere is pulled up in increments of 0.2 mm, stopped to take the image of contact line and moved up again. We let the interface to recede some amount before taking the data. The sphere is pulled up some amount in order to let the contact angle to escape from transient angles and pass to the fully receding case.

4.2.3 Analysis

The shape of the contact line of a sphere with the interface depends on shape of the liquid interface. If it is a planar liquid interface the contact line is in one plane
and circular. Figure 40 shows the contact line around the sphere at planar interfaces. It appears as a straight line in the image plane (front side). Assuming the contact line on the backside to be mirror image of the front side, 3-D image of the contact line is drawn.

![Side-view](image)

Figure 40: Side view of PDMS-coated sphere at planar liquid interface. In order to show that contact line is circular, 3-D plot is drawn by assuming backside of the sphere has the mirror image of the front.

However, when the same sphere is placed to a cylindrical interface, contact line around the sphere does not stay circular, it deforms from circular shape. The meniscus rises along one direction while it depresses along the other direction. This depends on shape of the interface: the meniscus moves along the direction of the principal curvatures along that direction (Figure 41). Changing the sign of the deviatoric curvature is equivalent to changing the sign of the quadrupole, as we confirmed in the experiments described below. Figure 41a and 41b show the water/air interfaces. Blue dashed line follows the interface. When the PDMS-coated sphere is placed (a=1.6mm), contact line will adopt to the interface shape (Figure 41c and 41d).
Figure 41: Cylindrical Interfaces. Interface and contact line is highlighted with blue dashed lines. a) Water/air interface in between 2 KOH washed glass slides. b) Water/air interface in between two razor blades. c,d) PDMS-coated glass sphere is dipped into those interfaces shown in a) and b).

From those images, pixel coordinates of the contact line are taken (Fig. 41c and 41d). Here, x-axis is defined perpendicular to the image plane, while y and z-axes are horizontal and vertical directions along the image plane, respectively. Since, y-z coordinates (stays in the image plane) and center and radius of the sphere is known, one can find all the information related with the contact line. Here, we plot the contact line $z \text{ vs. } \Phi$ (with respect to center of the sphere). Here, $z$ and $\Phi$ are the vertical position and azimuthal angle from polar coordinates.
Figure 42: z vs. Φ of contact line at cylindrical interface. Red line is the fit to the contact line (function is shown in Eq. 4.2). Sphere size a=1.6 mm.

The above figure shows the contact line in z- Φ plane. Φ ranges from −π/2 to π/2 (from left side of the image plane to right side). To find Φ,

\[ \Phi = \tan^{-1} \frac{y}{x}, \]

where x and y are the measured Cartesian coordinates of the contact line. For the given example in Figure 42, the contact line rises up and reaches maximum at Φ=0, and depresses almost symmetrically towards two sides. Around π/2 and −π/2, the contact line depresses and reaches minimum.

With our method, we can only observe the one half of the contact line around the sphere. The backside of the sphere is assumed to be a mirror image of the front
side. Thus, by this assumption we can predict the 3-D image of the contact line. This assumption is supported by the observation that the slope of the contact line is nearly zero at $\Phi = \pm \pi/2$, as required for a smooth line with front/back symmetry.

![Figure 43: 3-D extrapolation of contact line given in figure above. Sign of the quadrupole changes with the sign of the $D_0$.](image)

The figure above shows the 3-D image of the contact line at positive and negative deviatoric curvatures. Those plots nicely show us how contact line is deformed. The contact line is rising up and depressing along 2 perpendicular directions. Moreover, it switches sign when the sign of the deviatoric curvature change sign. The contact line is then fit to a multipole expansion function;

$$z(\varphi) = z_0 + z_1 \sin(\varphi) + z_2 \cos(2\varphi) + z_3 \sin(3\varphi) + z_4 \cos(4\varphi) + z_5 \sin(5\varphi)$$

This multipole expansion of the contact line gives us monopole ($z_0$), dipole ($z_1$), quadrupole ($z_2$) and higher terms. The monopole term, $z_0$, is the average height of the contact line. The dipole term $z_1$ gives us the tilt of the contact line from
horizon. Measured values of $z_0$, $z_1$ and $z_2$ under advancing and receding conditions are given below.

Figure 44: Multipole expansion of contact line. Filled and empty shapes are for advancing and receding cases, respectively. Square, triangle and star shapes represent monopole, dipole and quadrupole moments.

Here, $L_D$ was defined as the distance between the bottom of the sphere and undisturbed liquid interface. Since the $z_0$ term is moving as the sphere is pushed in or pulled out, contact line is not pinned. If it were pinned, the $z_0$ would stay constant.

Figure 44 shows $n=0$, 1 and 2 terms only, but what about the higher terms. We now, look at the higher terms in Equation 4.3.
Figure 45: Higher order of contact line deformation at cylindrical interface. \( n=3, 4, 5 \) terms are zero. \( D=0.12, a=1.6 \text{mm} \), sphere name: April6.

As seen in figure 45, \( n=3, 4 \) & 5 terms are indistinguishable from zero at cylindrical interfaces. Due to the symmetry of the contact line around the sphere at cylindrical interface, this is expected. What about the higher terms at saddle interfaces? Figure 46 shows that \( n=3, 4, 5 \) are non-zero unlike cylindrical interfaces.
4.2.4 Results

One of the first questions we ask is that whether the magnitude of the quadrupole \( z_2 \) is the same at different contact radius \( r_c \) and, if not, how they are related. In preliminary experiments, the relation between \( z_2 \) and \( r_c \) was first found linear. To change the \( r_c \), the sphere was pushed in more or pulled up, in order to reach to the intended configuration. However, with more careful experiments we have realized that \( z_2 \) depends on advancing and receding conditions, separately. Thus, we analyzed advancing and receding conditions, separately.
Figure 47: $z_2$ vs. $r_c$ of advancing and receding cases, separately. Filled and empty shapes correspond to advancing and receding cases. Cylindrical interface, $D_0=0.12\text{mm}^{-1}$, $a=1.6\text{mm}$. Sphere name: M27.

We find that the magnitude of the quadrupole is usually bigger in receding case compared to the advancing and it is not exactly linear with the contact radius (Figure 47). Here, the contact radius is calculated using $z_0$ from the fit function given in equation 4.3.

$$r_c = \sqrt{a^2 - z_0^2},$$

where $a = 1.6\text{ mm}$.

In fact, there is no prediction to explain how the induced quadrupole changes due to the capillary force. This force depends on the slope of the meniscus around the sphere. There is a prediction given by Zeng et. al for spheres, where the capillary
force on the sphere is zero (20, 44). According to this prediction magnitude of \( z_2 \) is related with the \( r_c \) and \( D_0 \) as,

\[
4.5 \quad z_2 = \frac{1}{6} D_0 r_c^2,
\]

However, this prediction is most appropriate for micron scale particles where gravity is negligible, \( aD_0 << 1 \).

As seen, this theory does not really apply to our case. There are four reasons: (1) there is a net external force on our spheres, (2) the size of our sphere is as big as the capillary length \( (L_c = 2.7\text{mm}, a=1.6\text{mm}) \), (3) the slope of the interface in these experiments is not always \( << 1 \) and (4) the measured contact angle is generally not the equilibrium Younge-Dupre value. Although there are many experimental work going on, there is no theory to explain all those results. Thus, to compare our results with the prediction given above, we extrapolated zero force case from our experiments by two different methods explained below. We extrapolated the zero force separately for advancing and receding cases.

We call the contact radius at zero force as \( r_c^0 \). As seen in figure 47, \( z_2 \) changes depending on \( r_c \). We call the magnitude of the quadrupole at \( r_c^0 \) as \( z_2^0 \). We have extrapolated \( r_c^0 \) by two methods which we describe as, 1) planar interface assumption and 2) force calculation from \( z(\Phi) \) and contact angle.

With the first method, we estimate when the meniscus around the sphere is planar. As the sphere is pushed in or pulled out, the meniscus has a tilt angle relative to the horizon, which determines the vertical force. With this method we find where (at what \( r_c \)) the tilt angle (\( \alpha \)) is zero. Thus, we can extrapolate the contact radius by approximating the interface as planar (horizontal), using the equation below.
$\phi = \pi - \theta_c + \alpha$

where $\theta_c$, $\alpha$, $\phi$ are contact angle, tilt angle (with the horizon), and the angle between the vertical axis of the sphere to meniscus (shown in Fig. 9, Chapter 1). This equation is true for planar liquid interfaces. Thus, this is an approximate method; it is not a direct way to find the zero force case. When $\alpha$ is zero, the capillary force at a planar interface is zero. For instance, in advancing case contact angle is $109^\circ$, and $\Phi$ is $71^\circ$, assuming tilt angle ($\alpha$) to be zero. Thus, the contact radius is $r_c = 1.6\cos(71^\circ) = 1.51$ mm. With this method, once the contact radius is found, we can read the corresponding $z_2$ from the $z_2$ vs. $r_c$ plot: $z_2 = 0.1$ mm at $r_c = 1.51$ mm (Fig. 48a). This is a rough calculation since the extrapolation of zero case is done from planar liquid interface. The reason we use this method is that we cannot observe the contact line when it is below the equator because of the contact angle restriction. At around $\theta_c = 90^\circ$, the contact line is at similar height with the undisturbed interface, and we cannot observe that point.

Figure 48: $z_2$ vs. $r_c$, separately. $D_0 = 0.21$ mm$^{-1}$, $a = 1.6$ mm. Sphere name: April6.
In the figure 48, \( z_2 \) vs. \( r_c \) is given for advancing and receding cases. For both cases, \( z_2 \) increases as \( r_c \) increases. Generally speaking, \( z_2 \) stays constant around the equator \((r_c = 1.6 \text{mm})\) for both advancing and receding cases. More discussion on \( z_2 \) and \( r_c \) will be given through the end of this section.

Now, we compare our results with this method to theory given by Zeng et al. The figure below shows our extrapolated results \( z_2^0 \) for advancing case at different \( D_0, z_2^0 \) vs. \( D_0(r_c^0)^2 \) is given. The example given in figure 48 is the last data point in figure 49.

![Graph comparing extrapolated \( z_2 \) and \( z_2^0 \) with theory](image)

Figure 49: Extrapolated \( z_{2,A}^{0} \) and comparison with the theory. These data were extrapolated by the method where the zero-force point was estimated by assuming a nearly planar interface.

Figure 49 compares \( z_2 \) under zero capillary force with the theory given by Zeng et al. Each point is taken from a different set of experiment at different \( D_0 \). The
straight line is the theoretical prediction. As seen our results agree very nicely with the theory. What about the receding case? In Figure 50, we show the $z_2^0$ vs. $D_0(r_c^0)^2$ both for advancing and receding cases and compare them with the theory.

![Graph showing $z_2^0$ vs. $D_0(r_c^0)^2$](image)

Figure 50: Comparison of the measured quadrupolar component (extrapolated from planar interface assumption) of the contact-line in advancing and receding cases at zero force with the theory of Zeng et al (straight line).

In figure 50, filled and empty shapes are the measured quadrupolar moments at zero force ($z_2^0$) in the advancing and receding cases, respectively and compared with the theory (solid line). Agreement of advancing case with the theory is very clear. Receding case separates away from the theory at higher $aD_0$. In theory, contact angle is the Young-Dupre angle, $\theta_{YD}$. Since, advancing case results are in better agreement with the theory, compared to receding case, we can conclude that advancing angle is closer to the $\theta_{YD}$. Moreover, even for receding case, as $D_0 r_c$ goes to zero, and difference between the prediction and the experiment diminishes.
On the other hand, these results support our results in chapter 2. In chapter 2, I showed that $\theta_R$ decreased as $D_0$ increased, while $\theta_A$ stayed constant. We concluded that this change in $\theta_R$ is due to the change in contact line shape at anisotropic interfaces. Here, with the analysis of the contact line around the sphere at anisotropic interfaces we show that magnitude of $z_2$ is bigger in receding case compared to advancing case. Bigger $z_2$ can cause a higher energy barrier for contact angle to reach to the equilibrium angle. This might be an explanation for why receding contact angle, $\theta_R$, decreases with increasing anisotropy. Moreover, since the measured $z_2$ for advancing agree very well with the theory, we concluded that advancing angle might be very close to the equilibrium Young-Dupre angle. This explains why advancing angle does not change as the anisotropy of the interface increases.

In the second method, we calculated the force on the sphere by knowing the contact line as a function of $z_n$, $\Phi$ and the contact angle. A python code used for these calculations is given in Appendix A. The units for calculating $F_{\text{cap}}$ are $\Upsilon^* r_c$, where $\Upsilon$ is the surface tension. For each advancing and receding case, at a given $L_D$ and $D_0$, the capillary force is calculated, separately. We now extrapolate $z_2^0$ when $F_{\text{cap}}=0$. 


Figure 51: $z_2$ vs. $F_{\text{CAP}}$ for both advancing and receding cases as the sphere is pushed in and out of the cylindrical interface. $D_0=0.21\text{mm}^{-1}$, $a=1.6\text{mm}$. Sphere name=April6.

From figure 51, we can extrapolate the $z_2^0$. This extrapolation is rather straightforward for receding case, since the planar interface case ($F_{\text{CAP}}=0$) corresponds above the hemisphere where, contact line is easily observed. However, advancing case corresponds to lower hemisphere, thus it is rather challenging to measure it. We extrapolate $z_{2,A}$ by assuming symmetric results around equator (Fig. 57). Thus, figure 51, tells us that $z_{2,A} = 0.12$ $z_{2,R} = 0.12$ at $F_{\text{CAP}}=0$. Then, we compare both methods.
Figure 52: Figure: Comparison of both methods used to extrapolate $z_2$ at zero capillary force. Square data is from planar interface assumption and star data is from force calculation methods.

The figure above compares the extrapolated $z_{2,A}$ from both methods. Square shape is the data extrapolated from the method described earlier and star shape is the extrapolated from the second method that was just described. As seen, both methods agree with each other and with the theory. Similarly, figure 53 shows the extrapolated $z_{2,R}$ from both methods. As $aD_0$ increases experimental data deviates away from the theory line.
Figure 53: Comparison of both methods used to extrapolate $z_2$ at zero capillary force for receding case. Square data is from planar interface assumption and star data is from force calculation methods.

Now, we turn to relation between $z_2$, $r_c$ and $F_{cap}$. There is no theory explaining how $z_2$ depends on $F_{cap}$ and $r_c$. Those relations can be studied using the method described above. We can calculate the capillary force on the sphere once we know the contact angle, the equation for the contact line, and we could try to understand its relation with $r_c$ and $z_2$. To start with, we look at how $F_{cap}$ changes at contact height of the contact line ($z_0$). The height $z_0$ is zero at the center, positive above the center and negative below the center of the sphere.
As seen, $F_{\text{CAP}}$ is always smaller for the receding case compared to advancing, at a given $z_0$. This is due to change in contact angle in the receding case. Basically, it is a geometric affect due to contact angle and contact height. In receding case, contact angle is smaller, so is the tilt angle and so is the capillary force.

In either cases advancing or receding, when $z_0$ approaches to 0, the equator, $r_c$ increases. Thus, we expect $F_{\text{cap}}$ to increase. However, as the contact line approaches to equator, $\alpha$ decreases due to the contact angle constriction. As $\alpha$ decreases, $F_{\text{CAP}}$ decreases as well. So, what would happen to the capillary force?
Figure 55: $F_{\text{CAP}}$ vs. $r_{c,A}$. Capillary force is calculated from the measured contact-line shape using the code given in Appendix A. $D_0=0.21\text{mm}^{-1}$, $a=1.6\text{mm}$. Sphere name=April6.

The figure above shows that the relation between $F_{\text{cap}}$ with $r_c$ is a nontrivial relation. Star shapes are the data points when contact line is below the equator. As the sphere is pushed in (advancing case), $r_c$ increases, at first (2 star shapes). Then, $r_c$ decreases as it is pushed in more (squares). At around $F_{\text{CAP}} = 3$, contact line is around the equator.
Figure 56: $F_{\text{CAP}}$ vs. $r_{c,R}$. Capillary force is calculated from the measured contact-line shape using the code given in Appendix A. $D_0=0.21\text{mm}^{-1}$, $a=1.6\text{mm}$. Sphere name=April6.

This figure shows that as $r_c$ increases (in receding case, pulling the sphere up), $F_{\text{CAP}}$ decreases. Square and star shapes are again refer to when contact line is above or below the equator.
Figure 57: $z_2$ vs. $z_0$ for advancing case. $D_0=0.21\text{mm}^{-1}$, $a=1.6\text{mm}$. Sphere name=April6.

Figure 57 is an informative plot to understand what $z_2$ depends on for advancing experiments. As seen at around equator, $z_0=0$, $z_2$ was maximum and stayed approximately constant. Figure 54 shows that, at that constant $z_2$, $F_{\text{cap}}$ increased from 1 to 5. Although the capillary force is increased, $z_2$ remained constant. On the other hand, at higher $z_0$, $z_2$ decreased as $F_{\text{cap}}$ increased. At those other points there is an inverse relation between the capillary force and the $z_2$. Let turn our attention to those points where $z_2$ stayed constant. Those points correspond to the equator, where capillary force makes an interesting shape with the $r_c$ in Figure 55. Moreover, there is a nice example in the receding case, shown in Figure 51; $F_{\text{cap}}$ changed sign from -2 to +2. For instance, at $F_{\text{cap}}=+2$, $z_2$ is 0.11, but at $F_{\text{cap}}=-2$, $z_2$ is 0.14. The magnitude of the capillary force stayed constant but just the
sign is changed. When we look at \( r_c \) at those two points it increases with \( z_2 \). This is interesting, because I would intuitively at first think that, at a given positive/negative capillary force, \( z_2 \) would be the same. Apparently, the relation between \( z_2 \) and \( F_{cap} \) is not that simple.

To summarize this section, we showed that at zero vertical capillary force, our results for the advancing case agree with the theory. For the receding case, \( z_2^0 \) was greater than predicted by the theory. We tried to extract the relation between \( z_2 \) and \( F_{CAP} \) from our experimental results, but this is rather a nontrivial relation. However, we could say that \( z_2 \) increases as \( F_{CAP} \) decreases and \( r_c \) increases. Around the equator (where \( r_c \) is maximum), \( z_2 \) is always maximum (Fig. 58).

![Figure 58](image-url)

Figure 58: \( z_2 \) vs. \( r_c/a \) is given for all the data sets for both advancing (filled shapes) and receding cases (empty shapes). \( r_c/a \approx 1 \) is the equator. Size of all spheres used is \( a=1.6 \text{mm} \).

### 4.3 Cylindrical particles at planar interfaces:

In this section, cylindrical particles are dipped into the planar liquid interface. A cylinder (purchased from McMasterCarr.com, Cat. No: 8496K1 &
8496K11) with diameter of 2-3 mm, made of heat-resistant borosilicate glass and coated with PDMS, is used. When the long axis of the cylinder was placed perpendicular to the planar interface, the contact line around the cylinder is smooth and contact line is measured the same on the left and the right sides, as will be shown below. However when the cylinder is dipped into the interface in a tilted way, contact angles on the right and left sides are not the same any more. This section provides a description of these experiments and the results.

Figure 59: Side and front view of tilted cylinder at water/air interface. Cylinder diameter is 3.2mm.
Figure 60: Hysteresis loop of cylinder oriented with its long axis perpendicular to the interface. Typical experiment starts with advancing the cylinder through the interface and then pulling it back up for receding case.

This figure shows hysteresis loop of the cylinder oriented with its long axis perpendicular to the interface. In this orientation, the contact line is symmetric, shaped like a circle. The meniscus around it is also symmetric, like a monopole. The measured advancing angle is $\theta_A = 108^\circ$ and the measured receding angle is $\theta_R = 100^\circ$. Those results are indistinguishable from our results at PDMS-coated glass spheres at planar interface (Chapters 2 and 3).

However, when the cylinder is placed in an orientation that is tilted in the plane of the image, the meniscus rises up along one direction while it depresses along the other direction. Thus, the contact line has the symmetry of a dipole. As the cylinder is tilted more, it makes a larger-amplitude dipole term in the contact line shape.
We checked how tilting the cylinder axis affects the advancing and receding contact angles. For figure 61, each time the cylinder was taken out, tilted in the plane of the image to an angle $\phi$ relative to the vertical, and then pushed into the interface. (Positive $\phi$ corresponds to clockwise rotation in the image plane.) Pushing the cylinder into the interface in perpendicular (to the planar interface) direction or along the tilt did not change our measurements. Those results are repeated twice for 3 different sizes (500um, 2mm, 3.2mm). For all sizes similar results are observed.

The measured $\theta_h$ are approximately antisymmetric in $\phi$, as expected (changing the sign of $\phi$ is equivalent to exchanging left side for right side.) When the tilt angle is about $\phi = 45^\circ$, $\theta_h$ is approximately $16^\circ$ larger on the right side than on
the left. As $\phi$ gets smaller the difference in contact angle between left and right sides decreases. Clearly there is a difference between the advancing contact angles on the left and right sides as the tilt increases. In particular, unlike the sphere experiments in chapter 3, $\theta_A$ differs from the planar-interface value. We will discuss this point below. The figure also shows the average of the left-side and right-side $\theta_A$ (black squares). We find that the average is remarkably steady at the planar-interface value.

Figure 62: Tilted cylinder at planar liquid interface. $\phi = 41.1^\circ$.

This figure shows an example of how the contact looks on the left and right sides. Here, $\phi$ is $41.1^\circ$, $\theta_L = 100^\circ$ on the left side and $\theta_R = 114^\circ$ on the right side. When the contact line is observed, we find that it makes an interesting shape with the interface. The figure below shows it in detail.
Figure 63: Contact line around the cylinder deforms from a planar shape when it is placed in tilted configuration. Advancing data, $\phi=41.1^\circ$. This image is the last data point in Fig. 55. The dashed line is drawn along the average height.

A straight line is drawn along the average contact height. This helps us to see the higher terms of multipole expansion (Eq. 4.3). Although we cannot see the whole shape of the contact line, we can roughly measure how much the contact line has been deformed from the blue line (average height). We find how much the contact line is deformed from average height. For this we measure the perpendicular distance between the blue line and the contact line at around $\phi=\pi/4$ ($\phi=0$ is the center of the cylinder). This is where the distance between the blue line and the contact line is maximum and it is a non-zero term (This term is called $z_4$ and shown in figure 64). If it were zero, contact line would follow the blue line and there would only be $n=0,1$ terms. However, since there is no symmetry around $\phi=0$, we eliminate $n=2$ term and at around $-\pi/4$ and $+\pi/4$ there is a minimum and maximum. Apparently there is a higher term causing the contact line to change its shape. Thus, the distance between the blue line and the contact line might be $n=3$ or
4 terms which goes as $z_3\sin(3\phi)$ and $z_4\cos(4\phi)$ in equation 4.3, or combination of both terms. (Please note that although it is plotted as $z_4$ on the y-axis, this term can be combination of $z_3$ and $z_4$.)

![Graph showing $z_4$ vs. $\phi$.](image)

**Figure 64: $z_4$ vs. $\phi$.**

Up to $\phi = 10^\circ$ the contact line has an elliptical shape. As seen from figure 61 the difference in $\theta_h$ between left and right sides appears around after $\phi = 10^\circ$, when the $z_4$ term starts to be obvious.

We have also looked at the receding angles on tilted cylinders in the same way. First, the cylinder was tilted, then pushed into the interface and pulled back up some amount, along its axis, made sure that the interface was fully receding.
Here, as the tilt ($\phi$) increases, $\theta_R$ decreases on both left and right sides. The values decreased from the planar-interface value of 100°, to about 85°. Those results might be compared to our results where $\theta_R$ decreased in value at anisotropic interfaces. When the cylinder was titled to 35°, $\theta_R$ decreased to nearly 85°. However, this set of experiments (only for receding case), needs to be repeated (There is only 1 reliable set of experiments for receding case, shown in Fig. 65).

The experiment above indicates that anisotropic shapes might have different contact angles around themselves. Although we do not have a full explanation for the changes in $\theta_A$ and $\theta_R$, we can make some comments based on the geometry. For instance, at $\phi = 35^\circ$, $\theta_A$ is 115° on the right side and 100° on the left side. If the contact angle were the same both on the left and right sides, what would the angle between horizon and the meniscus, $\alpha$, be?
Figure 66: Geometric argument for a cylinder at a planar liquid interface. Geometry is drawn and compared for constant angle ($\theta_L=\theta_R=108^\circ$) condition and experimental case ($\theta_L=100^\circ$, $\theta_R=115^\circ$).

The figure above shows the geometric argument of $\alpha$ in the case of constant and changing (experimental) contact angle cases. As seen if the $\theta_{A,L}$ and $\theta_{A,R}$ were the same, $\alpha_L$ and $\alpha_R$ are 53° and 17°, average $\alpha$ is 35°, the same as the tilt angle of the cylinder, $\phi$. In the case of constant contact angle $\theta=108^\circ$, both tilt angles on the left and right sides (53°, 17°) are bigger than the experimental ones (45°, 10°) where $\theta$ is 100°, 115° on the left and right sides.
Here, receding case at $\phi=35^\circ$ is compared. Both in hypothesized constant angle case and experimental case, average $\alpha = \phi = 35^\circ$. Unlike the advancing case, receding angles match on the left and right sides.

For advancing experiments, the data show that the change $\theta_A$ reduces the value of the horizon angle $\alpha$, which might also minimize the height of the interfacial deformation while preserving a constant average $\theta_A$ equal to the planar-interface value. For the receding experiments, the data show that the change of $\theta_R$ again reduces the height of the interfacial deformation, but this time the left and right sides remain nearly equal and the average $\theta_R$ decreases. This last result may have the same physical origin as the reduction of $\theta_R$ around spheres (Chapter 3). As $\phi$ increases, the higher term contribution to the contact-line increases and difference between in $\theta_A$ and $\theta_R$ increases (Fig. 65). Appearance of higher terms in contact line might explain change in contact angles in this chapter and in chapter 2. This raises the question, might the contact angle be a global constraint? Thus, contact angle
would adjust its value to minimize the total energy. This way, contact angle does not give a constant value (with some constraints that we do not know yet).

In order to explore other kinds of anisotropic shapes, an undergraduate student, Amanda LaFauci, working with us in Professor Dinsmore’s group, has successfully made ellipsoids from sphere by stretching them.

For future experiment, that would be very interesting to look at the following things:
1) To complete the experiments with the cylinder; different size of cylinders should be used such as between couple of hundred microns to 5 mm. At a given tilt angle $\phi$, as the radius of the cylinder increases how does the difference in left and right angles differ for advancing and receding cases?

2) Advancing and receding contact angles on the ellipsoids at 4 points, along the short and long axes can be measured. Since ellipsoids are made by stretching, it may be wise to coat them. For charge-stabilized spheres (of the type that are suspended in water), stretching can change the chemistry and roughness on the surface as pointed out previously (49). This might cause a variation in contact angle from an effect other than the interface shape. Coating the ellipsoids with PDMS may erase those problems.

3) Contact line around the ellipsoid can be measured and quadrupolar term can be measured from the image and compared to theory (52). If smaller ellipsoids can be made in time, those ellipsoids can be checked using optical profilometry.
4) Those ellipsoid can be placed on anisotropic interface in a way to see if the induced quadrupole from the interface can overcome the permanent quadrupole of ellipsoid.

4.4 Summary

In this chapter, two different types of experiments are done. In the first part, contact line around a PDMS-coated glass sphere is studied at anisotropic interfaces. Our experiments are the first ones where shape of the contact line can be observed directly. We showed that contact line around the sphere is different depending on whether the contact is advancing or receding. We measured the quadrupolar deformation, \( z_2 \), of the contact line from our images. Our measurements show that \( z_2 \) increases with \( r_c \) and \( D_0 \). Moreover, we tried to see the relation between the \( z_2 \) and capillary force on the sphere. This is not a trivial relation, but we believe our results will bring new questions and approach to this problem.

In the second part of this chapter, contact angle measurements of a cylinder are given. Advancing and receding contact angles are measured from left and right sides of the cylinder. Our results show that \( \theta_A \) is different on the left and right sides. And this difference increases as the tilt angle \( \phi \) increases. On the other hand, \( \theta_R \) did not show difference between left and right sides. However, \( \theta_R \) decreases as the \( \phi \) increases. We believe difference that the apparent advancing and receding contact angles show differences due to the deformation created at the liquid interface when it is tilted. Our results in this chapter support our contact angle results at anisotropic interfaces described in chapter 2. We have concluded in chapter 2 that the reason for apparent receding angle around a sphere to decrease is the
deformation in contact line. In this chapter, experiments with cylinders show that apparent contact angle can be affected by the contact line deformation.
CHAPTER 5

INDUCED REPULSION

5.1. Introduction

Colloids at liquid interfaces often either attract or repel each other (19, 73). This may depend on many things such as shape of the particles and of the interface (20, 44, 70) and wetting properties (intrinsic properties such as surface roughness and heterogeneity) (7, 45-51, 74-77). It is useful to treat the particles at liquid interfaces as charges and explain their attraction or repulsion by those charges by making analogy to electrostatic charges (69, 78-82). Shape of the particles would affect their charges and interactions with other particles at the interface.

In this chapter, an interesting observation is presented. It is known that two spheres would attract if they both are heavy or both are buoyant. Here we have two spheres, of which one is attached to a rigid rod and the other is left free to move at the interface. When the rod-attached one is pushed into the interface, the free sphere is attracted by the force field created by the rod-attached sphere and approaches to a definite separation where it comes to a rest. During this process, both spheres have meniscus in the downward direction. But, still the free sphere does not approach all the way to the rod-attached sphere and touch it. Instead, it stays at some distance. This is surprising because the simplest model of capillary forces would predict that two spheres that each makes a downward-sloped meniscus should monotonically attract one another.
In this chapter, I show experimental results and propose some future experiments that might explain our results and might likely be useful for the literature.

5.2 Experiments and Results

In those experiments two millimeter-sized spheres are used. One of the spheres is attached to a rigid rod with epoxy, by approaching from above. This process was described in detail in chapter 2. The sphere, which we call the rod-attached sphere, is dipped into the water/air interface at a controlled depth. The depth of the rod-attached sphere was defined as \( L_d \). On the other hand, the second sphere is placed to the liquid interface. It was free to move at the interface. As the depth changes, the meniscus around the rod-attached sphere changes. As the meniscus around the rod-attached sphere changes, the separation (edge-to-edge distance) between two spheres changes. The free sphere is attracted or repelled depending on the depth of the rod-attached sphere. In the following paragraphs details of the experiment are given.

We will describe two sets of experiments, in which we use two different kinds of particles for the rod-attached one (nylon, and then PDSM-coated glass). In the first experiments, the rod-attached sphere was made of nylon purchased from McMaster-Carr (part number: 9613K15) with diameter of 4.8mm. The free-floating sphere was PDMS-coated glass (details of PDMS coating and information of glass bead is given in chapter 2). As the rod-attached sphere is pushed into the interface, it deforms the interface (which we think of as inducing a curvature field around itself). The free sphere feels this field and aligns its position according to this field,
reaching a steady-state separation whose value changes with the depth of the rod-attached sphere. As the rod-attached sphere is pushed in more, the free sphere gets closer. The rod-attached sphere is pushed in, in increments of 0.05 mm on average. In the figure below (Fig. 68), a picture of two spheres at rest at their equilibrium separation is shown.

Figure 68: Nylon and PDMS-coated glass spheres further away from each other.

As seen in Figure 68, there is some distance between the rod-attached sphere (on the right) and the PDMS-coated free-floating sphere (on the left), although meniscus goes down near both spheres. Then, as the rod-attached sphere is pushed in, the free sphere approaches. The figure below (Fig. 69) shows the image when the rod-attached sphere is at a greater depth and the free sphere’s steady state position is closer.
Figure 69: Nylon and PDMS-coated glass spheres close to each other. Rod-attached nylon sphere on the right and PDMS-coated glass sphere on the left.

The figure shows when spheres are closer to each other. As seen, there is a very tiny distance in the spheres and still, they keep their separation. When the reverse process is done, pulling the rod-attached sphere up, a small amount of hysteresis was observed. Figure 70 shows the edge-to-edge distance between the two spheres vs. \( L_0 \), the depth of the rod-attached sphere. Data are shown for pushing in (advancing line) and pulling out (receding line) cases.
Figure 70: The edge-to-edge distance between a nylon rod-attached sphere and a free-floating PDMS-glass sphere is plotted vs. the depth $L_D$ of the rod-attached sphere. Different colors correspond to different trials using the same spheres. Black data points are for the first trial and others are repetitions without pulling the spheres out of the interface. Filled shapes are for pushing in and empty shapes are for, pulling out.

The plot above, shows that after the nylon sphere was pushed in, around 3.8 millimeters, the free sphere starts to feel it through the change in shape of the interface in between the spheres and comes closer to a separation of 3 mm. As the rod-attached sphere is pushed in 0.3 mm, two spheres touch each other. This process is reversible as seen above (Figure 70). The black data is from the first trial. In most of the experiments the first trial can show different results. This is due to, I believe, the change in wetting properties, as the sphere is pushed in. In the first trial,
the sphere is dry. As it is pushed in and out once, it may have a thin layer of liquid film on the surface. Thus, the following trials are different from the first one, but they are indistinguishable from the other following trials.

In those experiments, we can describe the interaction between those spheres as long-range attraction, short-range repulsion, which gives rise to a zero-force point at an intermediate separation. One might have expected those two spheres to be attracted to each other monotonically because of the monopole (isotropic) deformation around the rod-attached sphere and the free-floating heavy glass sphere (As seen in Figure 68, meniscus around each of the two spheres is sloped downward.) That is, if the rod-attached sphere were replaced by a heavy free-floating sphere then we should see monotonic attraction. Why is the result different when one of the spheres is attached to a rod? What is the reason for the observed short-range repulsion?

In order to understand this, we looked at the contact angle and contact line around the spheres, as well as the shape of the interface in between two spheres. For contact angle measurements we used PDMS-coated glass sphere as a rod-attached sphere. Thus, both free and rod-attached spheres are now coated with PDMS and have the same radius, \( a = 1.6 \text{mm} \). We will compare \( \theta_c \) and \( \alpha \) (angle of meniscus with the horizon) of the two spheres. First, we show the equilibrium separation of the two spheres at different \( L_D \).
Figure 71: Separation between two PDMS-coated spheres at different depth. The one on the left is attached to a rod. Both have the same radius, $a=1.6$ mm. In the second picture rod-attached sphere (on the left) is pushed in more, thus, free sphere (on the right) has approached.

Figure 71 shows two PDMS-coated spheres. One is attached to a rod (on the left) the other one is free to move around (on the right). As seen from figure 71, when the rod-attached sphere is at some depth free sphere is at some equilibrium distance. In the second picture, however, as the rod-attached sphere is pushed in more, free sphere has approached to the rod-attached sphere more. In order to understand the details of this unexpected phenomenon, we looked at the contact angles on the left and right sides of the free sphere; we observed that they are indistinguishable.
Figure 72: Contact angle of free PDMS-coated sphere as it approaches to the rod-attached sphere. Distance is from edge-to-edge. Squares and circles are contact angle on the left and right sides.

Our measurements show that $\theta_c$ of the free sphere is indistinguishable on the left and right sides. We now turn to measurements of $\alpha$. We found the shape of the interface using ImageJ, and measured the angle with the horizontal at the contact points on the left and right sides. The angle $\alpha$ is defined as negative if the meniscus slopes upward toward the sphere and positive if downward. The figure below shows $\alpha$ for free sphere. These measurements were made in steady state as the rod-attached sphere was moved step-by-step, either into the interface (increasing $L_D$ filled symbols) or out of the interface (open symbols). And the difference in horizon angle between left and right sides of the rod-attached sphere increases, as the free sphere is farther apart.
Figure 73: Change in horizon angle on the free sphere as spheres approach. Horizon angle on the left and right sides are given. Filled and empty shapes are for approaching and moving apart (but all measurements were made in steady state). Square and circles are contact angles on the left and right sides. Left side is closer to the rod-attached sphere.

For this data (Fig. 73), the rod-attached sphere was on the left side of the free sphere. Horizon angle, $\alpha$, on the left side of the free sphere (closer to the rod sphere) is smaller when spheres are far apart. This difference in $\alpha$ on the left and right sides can affect the vertical and lateral forces on the sphere. If we simplify by assuming the problem to be 1D (ignoring the forces and shapes out of plane), one can calculate the lateral force, which comes from the fixed force per unit length of contact ($\gamma$) and the orientation of the meniscus:

6.1 \[ F = 2\pi\gamma a \left[ \cos (\alpha_{\text{right}}) - \cos (\alpha_{\text{left}}) \right] \]
Since the $\alpha$ on the right side is bigger, the component of the force along the horizontal direction is smaller. Thus, total force is attractive and in order to understand the reason for equilibrium separation we look further into other parameters such as contact angles and contact line of spheres.

Now, we focus on rod-attached sphere. The figure below shows the $\theta_c$ of rod-attached sphere. 3 trials are done for measurements.

![Contact angle of rod-attached sphere](image)

Figure 74: Contact angle of rod-attached sphere (PDMS-coated, a=3.2mm). Squares and circles are for left and right sides, respectively (free sphere is on the right side).

The contact angle of the rod-attached sphere changes with $L_D$. The figure shows 3 trials with different colors. When the sphere is pushed in $L_D=1.6\text{mm}$ $\theta_c$ on the left and right sides are the same, $98^\circ$. However, when the sphere is pushed in further such as to $L_D=1.9\text{mm}$, $\theta_c$ on the left side remains the same, $\theta_c=98^\circ$. This is
the side where it is clear from any other particles. However, on the other side, closer to the free sphere, $\theta_c$ decreases to $82^\circ$. When the sphere is pushed down, the contact angle around the sphere is advancing. Thus, on the left side (free sphere is on the right) $\theta_c$ stays the same, however, on the right side $\theta_c$ decreases. This might mean that as the free sphere approaches to the rod-attached sphere the interface is receding from the rod-attached sphere. This is important information to understand the reason of repulsion. Possible reasons can be found in the discussion part.

Figure 75: Separation between two spheres at times separated by approximately 10 min. Both spheres are PDMS-coated glass, $a=3.2\text{mm}$. Free sphere is on the left and rod-attached sphere is on the right.

The above figure shows the separation between the two spheres in time. At time zero, two spheres are at some tiny separation. However, in time we have
observed that, the rod-attached sphere repels free sphere. To understand the reason we observe the change in contact angle and contact line around the sphere as well as the shape of the fluid interface between the spheres. The figure below shows the contact angles of the two spheres at these 3 separations are shown below.

Figure 76: Contact angles as the separation increases in time.

The figure above shows the contact angles of the rod-attached sphere (black) and free sphere (red) on the left and right sides. Difference in contact angle might be as mentioned before due to the change in height of the contact line around the sphere.

We try to explain our results by making analogy to electrostatic charges. As mentioned earlier, both free and rod-attached spheres have monopole in the same direction (interface deforming in the downward direction). Monopole term of free sphere is much bigger then the rod-attached sphere. This can be seen from the slope of the interface right before it touches the sphere. Thus, monopole interaction of
both spheres causes an attractive force. How about the dipole terms of the spheres? We now analyze the height of the contact line around the sphere on left and right sides. Figure 77 shows how \( w \) \((w=l-r)\) changes as the separation between the spheres changes. Here, \( w \) is the difference between left and right sides where distance is measured with respect to bottom of the sphere.

![Graph showing the height difference of left and right sides of the contact line](image)

**Figure 77**: Height difference of left and right sides of the contact line shown for the free sphere (red) and the rod-attached sphere (blue). In this plot, a positive value of \( l-r \) corresponds to a tilt in the clockwise direction.

Here, blue and red points belong to rod-attached sphere and free sphere. Negative \( w \) means that if a line is drawn from left to right side of the contact line on the given sphere, it is tilted in the counterclockwise direction. The difference in height of the contact line of the rod-attached sphere is always negative and increases as the separation increases. However, the difference in height of the contact line on free sphere is negative in the short-range and gets positive in the
long-range (very close to zero though). Interaction between dipolar terms of the spheres is repulsive in the first two images of figure 75 and weakly attractive for the third image. One has to compare the strength of the attractive and repulsive terms in order to make any conclusion. Here, we cannot make any exact solution but we can guess from the images that the possible repulsion is due to the dipole-dipole interaction of two spheres.

5.3 Discussion

What is the reason for the unexpected repulsion in the short-range between the two spheres? We still don't know the exact answer to this question, but we can rule out some possibilities and propose some explanations. To start with, we can rule out the contact angle. As evidence, when the rod-attached sphere is pushed in and pulled out, it has different contact angles due to hysteresis in contact angle and yet the steady-state separations are nearly indistinguishable. We know that hysteresis in the contact angle of PDMS-coated glass sphere at planar liquid interfaces is around 10-12 °. However, in both directions at a given $L_D$, the separation is the same. This is a good way to see that contact angle does not affect the separation between spheres.

We tried to explain our results with electrostatic analogy. Monopolar terms of both sphere is in the same direction, thus, it is attractive. For dipolar terms, as described above section, we focus on the contact line around the sphere and the interface between the spheres. The difference between the height of the left and right sides of the contact line on the rod-attached sphere changes sharply as the separation changes. We can define the difference between the height of left and
right sides on the contact line as tilt in contact line. A tilt of the contact line around the rod-attached sphere can be viewed as a tilt in the meniscus around that sphere, which corresponds to a dipole contribution to the meniscus shape. In the electrostatic analogy, this dipole will exert a force on the monopolar deformation around the free-floating sphere. This is analogous to the force between an electrostatic point charge and a dipole. The interaction between the dipole term of rod-attached sphere and the monopole of free sphere is attractive. However, interaction between dipolar term of free sphere and monopole of rod-attached sphere is repulsive. When those two terms are compared, latter is smaller than the previous term since dipolar term of the free sphere and monopolar term of the rod-attached sphere are very small. On the other hand, dipole-dipole interaction of spheres is repulsive in the short-range but attractive in the long-range.

For more detailed information, I have looked at the shape of the interface between the two spheres. The contact line around each sphere is not very clear. Thus, I have looked at the shape of the interface in between the spheres of the image below.
Figure 78: Interface shape between the two spheres in this image is analyzed. This image is the data point at d=21mm in the figure above.

Pixel coordinates of the interface were measured using ImageJ. Then those data points are fit to following function:

$$r = A \ln(r - r_c^F) + B \ln(r - r_c^R) + D (r - r_c^R)^{-1} + C (r - r_c^F)^{-1} + G (r - r_c^R)^{-1} + F (r - r_c^F)^{-2}$$

where \(r_c^F\) and \(r_c^R\) are the center of free and rod-attached spheres. The terms with A, D, C are the monopole, dipole and quadrupole of the rod-attached sphere while B, G, F are for free sphere. The result of the fit is shown in the plot below. Without the dipole and quadrupole terms of the function, the fit was not good near the rod-attached sphere.
The fit shows that dipole and quadrupole terms also contribute around the rod-attached sphere and the free sphere (D, C, G, F in the fits). Downward meniscus around the sphere is defined as positive in the fit. Thus, A and B terms are positive. Shape of the interface in between two spheres is not enough to make any conclusion. In order to fully understand the higher terms (dipole and quadrupole) we need to make a fit to the whole shape around the spheres.

In summary, in this chapter, an interesting, repeated and unintuitive interaction between two spheres is described. One of the spheres was free and the other one was attached to a rigid-rod. The meniscus around both spheres is curved in the same direction, which intuitively creates attraction between the two spheres. However, there is an equilibrium separation between the two spheres. Our analysis
shows that this may be due to dipole-dipole interaction between the spheres in the short range. For future experiments, following experiments can be useful; each sphere can be placed to the interface alone to measure the monopole terms at clean interface. For free sphere it is important to gently release it to the interface, since dropping the sphere on to the interface may cause force and change the monopole each time. Finding monopole term of rod-attached sphere is rather difficult, since it depends on the height of it at the interface. The more it is pushed in, stronger the monopole term is. Those terms should be used for monopole terms when the shape of the interface is analyzed. Moreover, analysis of the interface should be extended to the far side of both spheres not just between the two spheres. Those results are important for colloid interaction at fluid interfaces and self-assembly related problems.
APPENDIX

FORCE CALCULATION

In order to use this code, one needs to have “Python”. First put down the contact line equation $z(j)$ and contact angle into the code. To use the code, go to the folder where the .py folder is using the terminal and type -python documentname.py It will give the force on x,y,z coordinates.

```python
#!/usr/bin/python
# -*- coding: utf-8 -*-

#--------------------------------------------------------------
# Computes the surface tension force on a sphere from
# the shape of the contact line
# Input: shape of the contact line (or function)
# Output: force
#--------------------------------------------------------------
# 2014-06-18 Vincent Démery
#--------------------------------------------------------------

import numpy as np
import numpy.linalg as la

thetaC = 109.*(np.pi/180.)

nPts = 2000  # number of discretization points

def z(x):
    return (-0.13965-0.10262*np.sin(x)+0.05538*np.cos(2*x)-
    0.00551*np.sin(3*x)+0.00851*np.cos(4*x)+0.00306*np.sin(5*x))/1.6

#--------------------------------------------------------------
# Intermediate variables
#--------------------------------------------------------------
```

113
st = np.sin(thetaC)
ct = np.cos(thetaC)

def theta(phi):
    return np.arccos(z(phi))

# cross product of two vectors
def crossProd(a, b):
    c = np.zeros(3)
    c[1] = a[2]*b[0] - a[0]*b[2]
    c[2] = a[0]*b[1] - a[1]*b[0]
    return c

S = np.linspace(0.,2*np.pi,num=nPts)
R = np.zeros((nPts,3))
R[:,0] = np.cos(S)*np.sin(theta(S))
R[:,1] = np.sin(S)*np.sin(theta(S))
R[:,2] = np.cos(theta(S))
R1 = (R[:,1] + R[:,2-1])/2.
dR = R[:,1] - R[:,2-1]

N = np.zeros((nPts-1,3))
for i in range(nPts-1):
    N[i,] = crossProd(R1[i,], dR[i,])

F = np.zeros((nPts-1,3))
for i in range(nPts-1):
    F[i,] = (st*R1[i,]/la.norm(R1[i,]) - ct*N[i,]/la.norm(N[i,]))*la.norm(dR[i,])

f = np.sum(F,0)
print(f)
REFERENCES


33. Wenzel RN (1949) Surface Roughness and Contact Angle.1466--1467.


