Influence of the Drop Volume and Applied Magnetic Field on the Wetting Features of Water-based Ferrofluids

Barenten Suciu

Abstract—In this work, the influence of the drop volume and applied magnetic field on the wetting features of water-based ferrofluids is experimentally investigated. Firstly, water drops with volume ranging from 0.1–100 µL are placed on bare and coated acrylic plates, to gain reference data concerning the contact angle. Then, drops of water-based ferrofluid, with the volume ranging from 1 to 10 µL, are set on bare acrylic plates, which are placed into the uniform magnetic field created, in normal direction to the plate, by using permanent magnets. Since the ferrofluid drops are elongated along the magnetic field, the contact angle increases at augmentation of the magnetic flux. Besides, when a critical magnetic flux is exceeded, ferrofluid drop loose contact with the plate and jumps towards the magnet. A heuristic equation to predict the fluctuation of the liquid surface tension versus the drop volume, and also versus the ratio of the applied magnetic field energy to the kinetic energy of the magnetic particles dispersed into the water-based ferrofluid, is suggested.

Index Terms—Magnetic Field, Surface Tension, Contact Angle, Wetting, Water, Water-Based Ferrofluid, Drop, Micro-Pipette.

I. INTRODUCTION

Accurate information concerning the effects of electric and magnetic field on surface properties of drops is required to enhance various wetting technologies, such as spraying, painting, inkjet printing, separation, cleaning, and energy dissipation. Drops deformed by the electromagnetic field play a key role in numerous applications, ranging from micro-fluidic and mechatronic devices [1]–[8], to seismic and autovehicle absorbers [9]–[10], and to pharmaceutical or agricultural treatments [11]–[14].

In order to augment the influence of the applied electromagnetic field on the surface tension and contact angle, in many applications, pure liquids are often replaced by various electro-rheological or magneto-rheological fluids.

An extensive theoretical investigation upon the effects of magnetic and electric fields on the surface tension of liquids, followed by a critical discussion of various models found in literature, is delivered by [1]. Although the physical model, involving capillarity and electromagnetism for anisotropic fluid layers at mechanical equilibrium, is solved by quite an ingenious approach, the obtained integral expressions for the surface tensions are quite sophisticated to be used by the designer of micro-fluidic and mechatronic devices.

Alternatively, various heuristic equations, to describe the influence of magnetic and electric fields, were proposed based on measurements of the surface tension of magnetic fluids [2]–[3], water [4]–[5], conducting liquids, such as salted solutions [6]–[7], and polar liquids, such as alcohols [8]. Tested drops were placed on a variety of solid surfaces, such as PTFE, silicon wafers, polymeric materials, etc. Unfortunately, without explicit information concerning the wetting properties of the solid surface, and the size of the drops, the degree of confidence, and the effective range of applicability of such ad hoc formulae remain unsettled.

In this paper, based on Young’s equation of equilibrium for surface tensions, on state equations for interfacial tensions, i.e., on the relationship between the solid, liquid, and solid-liquid surface tensions, and on evaluation of contact angle during various wetting tests, a heuristic formula describing the fluctuation of the liquid surface tension versus the drop volume, and also versus the ratio of magnetic field energy to the kinetic energy of magnetic particles, is proposed.

In order to clarify the wetting features of the solid surface, firstly liquid drops of water, with the volume in the range of 0.1–100 µL, are placed in the absence of the magnetic field, both on bare and coated acrylic surfaces. Such coating is performed with trimethylsiloxyl, to alter the solid surface tension. Employing a technique that involves two overhead projectors and a camera, the contact angle of the quasi-circular water interface is measured. Then, drops of water-based ferrofluid, with the volume in the range of 1–10 µL, are placed on bare acrylic plates, and using the same technique, contact angle of the deformed liquid interface is determined, for various values of the magnetic flux density, applied in normal direction to the solid surface.

II. RELATIONSHIP BETWEEN THE FLUCTUATIONS OF THE LIQUID SURFACE TENSION AND THE CONTACT ANGLE

Data concerning the fluctuation of liquid surface tension versus the applied magnetic field is usually required by the designer of micro-fluidic and mechatronic devices. For this reason, it is generally provided by the theoretical models.

However, from an experimental standpoint, it is easier to measure the fluctuation of the contact angle Δθ/θ, and then, to find the corresponding apparent fluctuation ΔγL/γL of the liquid surface tension. Therefore, in this section, the relationship between the fluctuations of the liquid surface tension, and of the contact angle, is explicitly presented.

Firstly, employing the Young’s equation for the surface tensions equilibrium of a liquid drop on a solid wall (Fig. 1), the contact angle can be written as [11]:

$$\theta = \cos^{-1} \frac{\gamma_S - \gamma_{SL}}{\gamma_L}$$

(1)
Then, by using the equation of state for interfacial tensions [10–14], the solid-liquid $\gamma_{SL}$ surface tension can be expressed, versus the liquid $\gamma_L$ and solid $\gamma_S$ surface tensions, as follows:

$$\gamma_{SL} = \gamma_L + \gamma_S - 2\sqrt{\gamma_L\gamma_S} \exp[-\beta(\gamma_L - \gamma_S)^2]$$  \hspace{1cm} (2)

where $\beta$ is an empirical constant [14]. By substituting (2) into (1), the contact angle can be rewritten, only against the surface tensions of the liquid and solid phases, as:

$$\theta = \cos^{-1}\left[2\sqrt{\gamma_L\gamma_S} \exp[-\beta(\gamma_L - \gamma_S)^2] - 1\right]$$  \hspace{1cm} (3)

By differentiating (3) against $\gamma_L$ one finds the relationship between the fluctuations of the liquid surface tension and the contact angle, as:

$$\frac{\Delta \theta}{\theta} = \frac{\Delta \gamma_L}{\gamma_L} \times f(\gamma_L, \gamma_S)$$  \hspace{1cm} (4)

where the function $f(\gamma_L, \gamma_S)$ is given by:

$$f(\gamma_L, \gamma_S) = \frac{g(\gamma_L, \gamma_S) + \frac{1}{2} + \frac{1}{2} \gamma_L - \gamma_S}{g(\gamma_L, \gamma_S) - \frac{1}{2} \gamma_L + \gamma_S \cos^{-1}\left[2\sqrt{\gamma_L\gamma_S} \exp[-\beta(\gamma_L - \gamma_S)^2] - 1\right]}$$  \hspace{1cm} (5)

in which the function $g(\gamma_L, \gamma_S)$ is defined as:

$$g(\gamma_L, \gamma_S) = \sqrt{\gamma_S \gamma_L} \exp[-\beta(\gamma_L - \gamma_S)^2]$$  \hspace{1cm} (6)

![Fig. 1. Equilibrium of the liquid, solid, and solid-liquid surface tensions on a flat surface.](image)

III. RELATIONSHIP BETWEEN FLUCTUATION OF THE LIQUID SURFACE TENSION AND THE APPLIED MAGNETIC FIELD

Theoretical and experimental investigations on the liquid surface tension, when the applied magnetic field was parallel [2] or perpendicular [3] to the drop supporting solid surface, revealed that the fluctuation of the liquid surface tension can be written as a function of a dimensionless parameter $\alpha$, as:

$$\frac{\Delta \gamma_L}{\gamma_L} = h(\alpha)$$  \hspace{1cm} (7)

where $\alpha$ is defined as the ratio of the magnetic field energy to the kinetic energy of magnetic particles dispersed inside the ferrofluidic drop:

$$\alpha = \frac{B\nu B}{\mu_0\phi(1-\phi)kT}$$  \hspace{1cm} (8)

Here $B$ is the applied magnetic flux density, $B_s$ is the saturation flux density of the magnetic particles, $\mu_0$ is the magnetic permeability of vacuum, $V_0 = \pi d^2/6$ and $d$ are the volume and diameter of magnetic particles mixed into the water-based ferrofluid, $\phi$ is the volume fraction of the magnetic particles to the carrier liquid, $T$ is the absolute temperature, and $k$ is the Boltzmann’s constant. For the ferrofluid used in this work, the diameter and the volume fraction of magnetic particles are $d = 10$ nm and $\phi = 0.03$.

Thus, under a magnetic field applied parallel to the drop supporting solid surface, for a water-based ferrofluid, the drop was elongated from a circular top-view shape to an elliptical top-view shape [2]. In such conditions, function $h(\alpha)$ was fitted to the following power-type form [2]:

$$h(\alpha) = 0.0025 \times \alpha^{0.8}$$  \hspace{1cm} (9)

However, the shape of the fitting function is still to be clarified for various sizes of the drop, and also for the case when the magnetic field is applied perpendicular to the drop supporting solid surface. Therefore, in order to clarify such aspects, several wetting tests are performed, as discussed in the following sections.

IV. TEST RIG AND EXPERIMENTAL PROCEDURE

By employing micro-pipettes, drops of pure water and water-based ferrofluid with the volume $V$ varying in the range of 0.1–100 µL were placed on solid acrylic plates. Relative error upon the drop volume was of ±12 % for $V = 0.1–0.5$ µL, of ±2.5 % for $V = 0.5–10$ µL, and of ±3 % for $V = 10–100$ µL. Corresponding radius $R$ of the drop, before setting on the solid wall, varied in the range of 0.29–2.88 mm. For easy visualization of the drop shape on the solid surface, section paper with a pitch of 0.5 mm was placed beneath the transparent acrylic plate (Fig. 2).

Surface tension of water during tests at an environmental temperature of 24 °C was $\gamma_L = 0.072$ N/m.

![Fig. 2. Photograph of the employed orthogonally disposed acrylic plates](image)
black colloid, containing iron particles with a diameter of about 10 nm, mixed in water. Its physical properties, found at the same environmental temperature of 24°C, are listed in Table I.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.190 kg/m³</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>0.005 Pa·s</td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.057 N/m</td>
</tr>
<tr>
<td>Saturation magnetic flux density of ferrous particles</td>
<td>18.5 mT</td>
</tr>
</tbody>
</table>

Fig. 3 illustrates a schematic view of the contact angle measurement equipment used in this work. Two overhead projectors (OHP1 and OHP2) are used to capture the top-view (OHP1 in Fig. 3) and the frontal-view (OHP2 in Fig. 3) of the liquid drop placed on the acrylic solid surface. Obtained images are projected on a vertical screen, and then, captured by using a high performance camera, to gain a magnification factor of 20. Using this technique, the proximity of the measurement equipment to the tested drop, and also to magnetic field can be avoided. Magnetic field, acting on normal direction to the plate, is created by using permanent magnetic disks (Fig. 4).

As detailedly shown in the next section, the frontal-view shape of the drop on the solid surface might be quasi-circular in the case of pure water (Fig. 5), or quasi-triangular in the case of water-based ferrofluid (Fig. 6). Thus, under the radial symmetrical magnetic field, the drop is elongated along its longitudinal axis, and consequently, it is displaying a larger apparent contact angle. One emphasizes that the contact angle might be evaluated as \( \theta = 2\tan^{-1}(2a/b) \) in the case of quasi-circular shape (Fig. 5), or as \( \theta = \tan^{-1}(2a/b) \) in the case of quasi-triangular shape (Fig. 6), where \( a \) and \( b \) are the height and the mean diameter of the liquid drop placed on the solid surface, respectively.

Contact angle measurements were conducted both on the bare and coated acrylic surfaces. Coating is performed with the commercially available trimethylsilyl (–Si=O(CH₃)₃). The slight reduction of the solid surface tension, achieved in this way, produces an increased liquid-repellency level of the acrylic surface.

V. RESULTS AND DISCUSSIONS

A. Contact Angle of Water Drops on Acrylic Surfaces

Fig. 7 illustrates the frontal-views and Fig. 8 shows the top-views of various water drops with the volume varying in the range of 0.1–100 µL, placed on the bare, i.e., uncoated acrylic solid surface. Similar results of higher contact angle were obtained for the coated surface, due to its augmented liquid-repellency.

Fig. 7. Frontal-views of water drops with the volume varying in the range of 0.1–100 µL, placed on bare, i.e., uncoated acrylic solid surface.
One observes that larger drops spread over a wider area, but the shape of the liquid-solid interface appears as quasi-circular both in the frontal (Fig. 7) and top (Fig. 8) views. In conclusion, the interface rapidly reaches on the solid surface an equilibrium position which minimizes its potential energy.

Since the frontal-views of the water drops from Fig. 7 are similar to those shown in Fig. 5, one firstly determines the height $a$ and the mean diameter $b$ of the liquid drop, and then, calculates the contact angle as $\theta = 2 \tan^{-1}(2a/b)$.

Results obtained are illustrated in Fig. 9, which presents the variation of the contact angle $\theta$ versus the volume $V$ of the water drop, obtained both for the uncoated and coated acrylic solid surfaces.

As expected, higher contact angle is found on the coated surface, due to its increased water-repellency produced by the trimethylsilyl groups applied on the acrylic plate. On the other hand, the contact angle parabolically decreases at the augmentation of the water drop volume. Such effect is caused by the increased weight of the drop, which has to be supported by the elastic spring-like liquid-solid interface.

Various functions to fit the experimental results shown by Fig. 9 were tested, but the best fitting, corresponding to a correlation coefficient $R^2$ higher than 0.8, was achieved for the following quadratic polynomial curves:

$$\theta = \Delta \cdot V^2 + \Phi \cdot V + \Gamma$$

Since the first two polynomial coefficients $\Delta$ and $\Phi$ have the same values ($\Delta = 0.002 \text{deg}/\text{m}^2$, $\Phi = -0.33 \text{ deg}/\text{m}^2$) for both the coated and uncoated acrylic surfaces, it seems that they are merely expressing the influence of the drop volume on the contact angle. Besides, the coefficient $\Gamma = \theta(V = 0)$ appears to be the true contact angle, which is uninfluenced by the drop volume. As expected, the true contact angle displayed by the coated surface ($\Gamma = 75.3 \text{ deg}$) is larger than that corresponding to the uncoated surface ($\Gamma = 67.2 \text{ deg}$).

Next, by substituting the values of the true contact angle and the water surface tension $\gamma_L = 0.072 \text{ N/m}$ in (3), one determines the solid surface tension as: $\gamma_s = 0.0474 \text{ N/m}$, for the coated plate, and $\gamma_s = 0.0507 \text{ N/m}$, for the uncoated acrylic plate. Such findings are in range of values previously reported for the polymer-liquid interfaces [11]-[14].

Results obtained for water (Figs. 7-9) illustrate that the range of $V = 0.1$–100 $\mu$L for the drop volume, initially selected for investigation, is too wide. On one hand, the contact angle for $V = 0.1$–1 $\mu$L displayed large scattering (Fig. 9), presumably produced by the lower accuracy of the micro-pipette in this range. On the other hand, the contact angle for $V = 10$–100 $\mu$L is chiefly influenced by the drop volume, since large drops disperse over a wide area, and, produce liquid film on the surface. For these reasons, in the following tests, involving the ferrofluid drops, the volume is limited to a narrower range of $V = 1$–10 $\mu$L.

### B. Contact Angle of Ferrofluid Drops on Acrylic Surfaces

Fig. 10 illustrates the top-views, and Fig. 11 shows the frontal-views of various ferrofluid drops with the volume varying in the range of $V = 1$–10 $\mu$L, placed on the uncoated acrylic solid surface. Flux density of the magnetic field was set to one of the following values: $B = 0, 20.15, 21.55, 21.85, 23, 24.5, 24.9, 27.4, 27.8, 28.3, 30.1, 30.6$, and $31.5 \text{mT}$. Frontal-view shape of the ferrofluid drop is quasi-circular in the absence of the magnetic field, as shown by the first row of photos in the left side of Fig. 11. As the magnetic field is increased, drop shape changes towards a quasi-triangular pattern, as shown by the photos in the right side of Fig. 11. Such shape change occurs at lower values of the magnetic flux density if the volume of the liquid drop is increased. Accordingly, after evaluation of the height and mean diameter of the liquid drop, the contact angle should be calculated with the proper relationship $\theta = \tan^{-1}(2a/b)$, which was indicated by Fig. 6.

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**Fig. 8.** Top-views of water drops with the volume varying in the range of 0.1–100 $\mu$L, placed on bare, i.e., uncoated acrylic solid surface.

**Fig. 9.** Variation of the contact angle versus the drop volume for water drops placed on uncoated and coated acrylic solid surfaces.

**Fig. 10.** Variation of the contact angle versus the drop volume for ferrofluid drops placed on uncoated acrylic solid surfaces.
Concerning the contact angle, by substituting the values of the ferrofluid surface tension \( \gamma_f = 0.057 \text{ N/m} \) and the solid surface tension \( \gamma_s = 0.0507 \text{ N/m} \) in (3), the true contact angle of ferrofluid drop on the uncoated acrylic plate becomes \( \theta = 31.2 \) deg. This computed value agrees with the experimentally obtained result illustrated by Fig. 12.

Thus, Fig. 12 shows the variation of contact angle versus the applied flux density of the magnetic field, for various values of the drop volume. Since the drops are elongated along the magnetic field, the contact angle increases at augmentation of the magnetic flux density, for tests in the range of \( B \geq 20.15 \text{ mT} \), and such effect is more prominent at larger values of the drop volume.

When the magnetic field reaches a certain critical level, the ferrofluid drop loose contact with the acrylic surface and jumps towards the magnet. This means that the attraction force exerted by the magnet exceeds the resultant force of the drop weight and the attractive force between the acrylic solid surface and the drop. Critical magnetic flux density parabolically decreases at augmentation of the drop volume, as illustrated by Fig. 13.

![Fig. 10. Top-views of various ferrofluid drops with the volume varying in the range of 1–10 µL, placed on uncoated acrylic surface (Magnetic flux density, \( B = 0 \text{ mT} \)).](image)

![Fig. 11. Frontal-views of various ferrofluid drops with the volume varying in the range of 1–10 µL, placed on uncoated acrylic surface (Magnetic flux density, \( B = 0 \text{ mT} \)).](image)

![Fig. 12. Variation of the contact angle versus the magnetic flux density (Drop volume, \( V = 1, 3, 5, 7, 9 \mu\text{L} \)).](image)

![Fig. 13. Variation of the critical magnetic flux density versus the ferrofluid drop volume.](image)

Fig. 14 shows the experimentally obtained fluctuation of the liquid surface tension \( \Delta \gamma_L / \gamma_L \) versus the dimensionless parameter \( \alpha \), which represents the ratio of the applied magnetic field energy to the kinetic energy of the magnetic particles dispersed into the water-based ferrofluid. Curves shown in Fig. 14 can be approximated quite well, i.e., with a quite high correlation coefficient of \( R^2 = 0.999 \), by a function of two variables \( (\alpha, V) \), and more precisely, by a function implying the multiplication of \( \alpha \) with a quadratic polynomial function of \( V \), as follows:

\[
\frac{\Delta \gamma_L}{\gamma_L} = \alpha(\alpha^2 - 2.67\alpha + 1.74)(9.1V^2 - 25V + 71.5)
\]  

(11)

Such multiplication of functions with separate variables, precisely describes the condition of nil fluctuation of the liquid surface tension in the absence of the magnetic field \( (B = 0) \):

\[
\frac{\Delta \gamma_L}{\gamma_L} (\alpha = 0, V) = 0
\]

(12)

Moreover, (11) predicts the true variation of the liquid surface tension versus the magnetic field, i.e., the change in the liquid surface tension of an infinitesimal liquid drop due to the applied magnetic field, as follows:
\[ \frac{\Delta \gamma_L}{\gamma_L}(\alpha, V = 0) = 71.5\alpha(\alpha^2 - 2.67\alpha + 1.74) \]  \hspace{2cm} (13)

Additionally, the fitting function (11) precisely predicts for the value \( \alpha \approx 1.3 \) the points of minima observed on Fig. 14, for the \( \Delta \gamma_L / \gamma_L \) fluctuation curves, corresponding to lower drop volumes of \( V = 1–5 \) µL.

VII. CONCLUSION

Heuristic equations to take into account the influence of water drop volume, as well as the influence of ferrofluid drop volume and applied magnetic field on the contact angle and liquid surface tension, were obtained based on wetting tests. Firstly, drops of pure water, with the volume in the range of 0.1–100 micro-liters, were placed by using micropipettes on bare and coated acrylic plates, to gain reference data regarding the contact angle. Then, drops of water-based ferrofluid, with the volume in the range of 1–10 micro-liters, were set on bare acrylic plates, which were placed into the uniform magnetic field, created in the normal direction to the solid surface, by using magnetic discs. Following main conclusions could be inferred from the performed study.

1) Contact angle parabolically decreased at augmentation of the water drop volume. This might be explained by the fact that, in order to support the increased weight of larger drops, the elastic spring-like liquid-solid interface has to disperse over a wider area, and to produce liquid film on the surface. Such spreading process affects the cohesion of liquid molecules and generates a distortion of the interface towards lower contact angles.

2) Since the polynomial coefficients corresponding to the water drop volume and square volume are unaffected by the coating of the acrylic surface, it appears that they are merely expressing the influence of the drop volume on the contact angle. Besides, the third coefficient of the parabolic function seems to be the true contact angle, which is uninfluenced by the drop volume, but depends on the solid surface tension.

3) Frontal-view of the ferrofluid drops is quasi-circular in absence of the magnetic field, but as the magnetic flux density is increased, the drop shape changes towards a quasi-triangular pattern. Such shape change occurs at lower values of the magnetic flux density, if the volume of the liquid drop is increased.

4) Since ferrofluid drops are elongated along the magnetic field, the contact angle increases at augmentation of the magnetic flux density, and the effect is more prominent at larger values of the drop volume.

5) When the magnetic field reaches a certain critical level, the ferrofluid drop loose contact with the acrylic surface and jumps towards the magnet. Such critical magnetic flux density, under which the drop levitation can be achieved, parabolically decreases at augmentation of the drop volume.

6) Proposed heuristic equation describes quite accurately the fluctuation of the liquid surface tension versus the drop volume (quadratic polynomial function), and also versus the ratio of the applied magnetic field energy to the kinetic energy of magnetic particles dispersed into the ferrofluid (cubic polynomial function).

VI. NOMENCLATURE

\( a \)  Height of the drop on the solid surface, [m]
\( b \)  Mean diameter of the drop on the solid surface, [m]
\( B \)  Magnetic flux density, [T]
\( B_c \)  Critical magnetic flux density, [T]
\( B_s \)  Saturation magnetic flux density, [T]
\( d \)  Diameter of the ferrofluid magnetic particle, [m]
\( k \)  Boltzmann’s constant, 1.38\times10^{-23} [J/K]
\( R \)  Drop radius formed by the micro-pipette, [m]
\( T \)  Absolute temperature, [K]
\( V \)  Drop volume, 4\piR^3 / 3 [µL, m^3]
\( V_o \)  Diameter of the ferrofluid magnetic particle, \( \pi d^3 / 6 [m^3] \)
\( \alpha \)  Ratio of the magnetic field energy to kinetic energy of magnetic particles, \( B_s V_c B / (\mu_0(1 - \phi)kT) [-] \)
\( \beta \)  Constant in the equation of state for interfacial tensions, [(m/N)^2]
\( \phi \)  Volume fraction of magnetic particles to the liquid carrier, [-]
\( \Delta \)  Fitting coefficient describing the influence of drop volume on the contact angle, [deg/m^6]
\( \Phi \)  Fitting coefficient describing the influence of drop volume on the contact angle, [deg/m^3]
\( \Gamma \)  Fitting coefficient denoting the true contact angle, [deg]
\( \gamma_L \)  Liquid surface tension, [N/m]
\( \gamma_s \)  Solid surface tension, [N/m]
\( \gamma_{SL} \)  Solid-liquid surface tension, [N/m]
\( \mu_0 \)  Magnetic permeability of vacuum, \( 4\pi \times10^{-7} [N/A^2] \)
\( \theta \)  Contact angle, [deg]

REFERENCES
