Retention Dynamics of Droplets over Compliant Substrates

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Abstract

Droplet dynamics over substrates hold numerous applications including Fuel cell technologies, anti-icing, and cleaning technologies. However, fundamental understanding of droplet retention over compliant substrates has not received much attention. This paper presents a detailed investigation of the effect of substrate compliance over contact angles and maximum retentive/adhesive force applied over the droplet by a substrate (of varying degrees of compliance). We have defined a non-dimensional number called “Substrate Compliance (C_s) as C_s = \frac{\gamma P_t + \rho V g t}{F}$, which can act as the parameter representing the degree of compliance of the substrate.

An analytical model is developed to determine the maximum retention force applied over the droplet, which could predict the retention force offered by the substrates (with $0 < C_s < 12000$) satisfactorily with a maximum deviation of 11.52% from experimental results. Further, the effect of substrate compliance over contact Angle Hysteresis (CAH), the shape of the droplet, and retention force has been investigated. CAH of droplets over a compliant substrate is found to be higher ($\geq 200\%$ at inclination angle $= 30^\circ$) with more elongation and aspect ratios as compared to a non-compliant substrate. Also, a free-hanging thin Polydimethylsiloxane (PDMS) membrane (a compliant substrate) could retain $\sim 146 - 276\%$ higher droplet volumes compared to a PDMS-coated glass substrate.

In the end, we have developed and employed an Artificial Neural Network (ANN) model to predict the stiffness of PDMS membranes using experimental data, which is successful with an overall $R = 0.90$.

Keywords: Substrate Compliance, Droplet Retention, Contact Angle Hysteresis, Artificial Neural Network

1. Introduction

Surface tension allows liquid drops to cling to sloped or vertical surfaces. Calculating the net adhesion force between a droplet and a solid surface is necessary for many applications including areas such as fuel cell technologies, wind turbines, cleaning, and anti-icing applications [1-5]. To ascertain the circumstances of a liquid droplet’s displacement over an inclined solid surface under the impact of body force like gravity, numerous investigations have been carried out. Friction force or retention force are terms used to refer to the lateral force necessary to overcome the interfacial shear resistance between a liquid droplet and a solid surface [6]. Various experimental methods, including the inclined plane technique [7-9], centrifugation technique [10,11], and direct dragging technique [6], have been used in the past to investigate the sliding behavior of droplets on solid surfaces. For a wide range of advancing and receding angles and Bond number values, Dimitrakopoulos and Higdon (1999) presented numerical data for the maximum adhering force of a droplet on a surface [12]. A theoretical model developed by Furmridge (1962) links the contact angle hysteresis to the force required to hold a droplet on a tilted surface [13]. Retentive forces were measured for various liquid-surface combinations and were then connected to drop geometry by Extrand et al. [14, 15]. When retaining a critical drop, the surface tension force, $F_s$, can be related to the contact angles by

\[ F_s = \frac{\gamma}{\cos \theta_a - \cos \theta_r} \]

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In this equation, $k$ is a constant, $\gamma$ is the liquid-vapor surface tension, $R$ is the length scale that represents the size of the drop contour, and $\theta_A$ and $\theta_R$ are respectively, the advancing and receding contact angles. The shape of the drop affects the factor $k$. Estimates of $k$ have varied by more than 300% due to disagreements in the literature on contact-angle distributions in drops and contour shapes.

When gravitational force (or any other body force) exceeds surface tension—the threshold of incipient motion—a drop reaches a critical condition. An increase in drop size or surface inclination might result in such a situation. The behaviors of solid surfaces can also greatly alter how they retain liquid over them [17-18]. For instance, despite the high static contact angles of both lotus leaves and rose petals, water droplets readily move on one surface while securely sticking to the other due to the radically different surface microstructures [17].

All these above-mentioned studies were conducted on droplets resting over solid substrates which weren't compliant. Due to compliance of the substrate, a considerable distortion of an elastic thin film in the form of a bulge can result on the opposite side due to the Laplace pressure of a droplet applied on one side of the film [18]. Schulman et al. (2015) [19] have investigated the deformation caused by micro-droplets on top of thin, free-standing films made of elastomer. They observed that as a result of the bulge created in the membrane, two angles; one made by the deformed bulge with the deformable thin elastomer film and the second made by the liquid surface with the air, define the droplet or membrane shape. Further, the effects of compliance on the contact angles between the droplet and substrates, as well as the stresses produced inside the membrane have also been studied by Nadermann et al. (2013) [20]. Though, these literatures studied the droplets resting on a compliant membrane, the investigation on the adhesive or, the retentive force experienced by the droplet over a thin inclined free-hanging compliant membrane has not been investigated to the best of our knowledge.

In this paper, a comprehensive investigation of the retention dynamics of droplets over inclined substrates of varying degrees of compliance ranging from completely rigid to free-hanging deformable membranes has been carried out. A theoretical model is developed using fundamental geometry principles, which can determine the net retentive force faced by droplets placed over rigid as well as compliant inclined substrates. In this model, the droplet contact line is considered axisymmetric and is made up of segments from two distinct ellipses with the same minor axis. The developed approach has taken inspiration from the microscopic images of droplets resting over substrates of varying compliances. The theoretical model has been validated with the experimental data. Thus, the effect of substrate compliance over the forces experienced by droplets is investigated.

Next, the reaction force experienced by the compliant substrate is analyzed. Here, theoretical modeling of deformation and/or bulge in the inclined free-hanging thin membrane (due to the forces from the droplet) is challenging because of the complex nature of governing equations. Towards this, artificial neural network (ANN) models can be one of the best choices to relate the compliance wall deformation with the droplet and interfacial properties due to their simplicity and low computational cost. ANNs are computer algorithms that seek to imitate the functioning and decision-making processes of the human brain [35], and they have become the focus of numerous scientific investigations. ANNs have been used to forecast various parameters in different studies, including material characteristics [36], cell properties [37], and hydrological processes [38-39] with great effectiveness. Hence, in the last part of the work, we have trained and tested an ANN model to relate the parameters from droplet retention with the membrane material properties.

The paper is outlined as follows. First, the theoretical approach to model the contact line of the droplet resting over an inclined surface is elucidated. Then, the surface forces acting on the contact line at three distinct interfaces are analysed for substrates of distinct
compliances. Further, the analysis of the total retention force acting on the droplet is presented. Then, the role of the artificial neural network (ANN) model to predict the composition of membranes by utilizing its deformation characteristics is explained. Finally, the validation of the theoretical model with experiments has been presented in detail. In the end, the predictions of ANN are reported.

2. Materials and Methods

Figure 1 shows the four types of surfaces used for the investigation in the current work which is as follows.

(i) **Polymethylmethacrylate (PMMA) block** ($S_{PMMA}$) of thickness 0.3 cm is used for modeling completely rigid substrates (Fig. 1(a)). $S_{PMMA}$ would be used for representing this substrate throughout the manuscript.

(ii) **Soft elastomer Polydimethylsiloxane (PDMS) coated glass substrate** ($S_{PCG}$) is used for modeling substrates with rigid bulk material with soft surfaces (Fig. 1(b)). The thickness of the coated thin PDMS layer was kept at 20–70 μm. $S_{PCG}$ would be used for representing this substrate throughout the manuscript. Here, $PCG$ stands for PDMS-coated glass.

(iii) **PDMS block** ($S_{PB}$) is used for modeling substrates with soft bulk material with soft surfaces Fig. 1(c)). The thickness of the PDMS block was kept at 0.8 ± 0.1 cm. These substrates were soft, but not compliant. $S_{PB}$ would be used to represent this substrate throughout the manuscript. Here $PB$ in the subscript stands for PDMS block.

(iv) **Thin free-hanging PDMS membrane** ($S_{PM}$) of thickness 20–700 μm is used for modeling soft-compliant substrates Fig. 1(d)). $S_{PM}$ would be used to represent this substrate throughout the manuscript. Here, $PM$ in the subscript stands for PDMS membrane.

As visible in figure 1d, the PDMS membrane was bonded onto a diced PDMS block such that the membrane is free hanging. In contrast to PDMS blocks, these substrates are soft and compliant. The dimensions of the free-hanging part of the membrane were adopted such that they caused the least amount of pre-stress and sagging in the fabricated membranes. Also, these smaller dimensions of the membrane could allow the fabrication of comparatively thinner membranes of thickness as low as 20 μm. Please refer to figure 3b for the microscopic image of a cross-section of one of the fabricated thin PDMS membranes.

The choice of PDMS was based on its ease of manufacture of thin membranes and capacity to provide a wide range of elasticity for various applications [21]. The PDMS was acquired from Dow Corning, USA, and was used to fabricate blocks, layers deposited on glass slides, and membranes attached to the blocks. A large number of samples were fabricated and substrates with varying thicknesses within a certain range were chosen for comparison. Two types of liquid droplets, distilled water and droplets with 60% glycerol in water (w/w) were used for the experiments. The values of $Y_{la}$, $Y_{li}$, $Y_{as}$ for water, aq. glycerol, PDMS, and PMMA were taken from existing works of literature [32-34].

2.1 Device Fabrication

PMMA blocks were cut into specified sizes for the $S_{PMMA}$ substrate. For the fabrication of $S_{PCG}$, glass slide (of thickness 1.45 mm, Blue Star, Polar Industrial Corp., India) were coated with a thin PDMS layer by placing a small amount of elastomer-curing agent mixture with a 10:1 ratio and rotating at 1500 – 3500 rpm using a Spin-Coater (Deltaspin-1, Delta Scientific India). The coated glass slide was then baked for 90 min at 80°C in a hot air oven (NSW-129, Narang Scientific Works, India). The solidified PDMS-coated glass was then removed from the oven, allowed to cool, and then used as $S_{PCG}$ substrate. For substrate $S_{PB}$, liquid mixture of an elastomer-curing agent with a 10:1 ratio, was baked for 90 min at 80°C and cut into specified sizes shown in figure 1c. Further, the fabrication steps of the substrate $S_{PM}$, are described below. First, thin PDMS membranes were fabricated by spin-coating liquid PDMS over a PMMA sheet at rotational speeds ranging from 700 – 3000 rpm, and baking it at 80°C for 90 min in a hot air oven. Also, PDMS blocks were fabricated and diced into specific dimensions (shown in figure 1d). Then, the PDMS-coated PMMA sheet and diced PDMS block were subjected to air plasma for one minute at 0.2 Torr pressure using a Plasma Cleaner (PDC02, Harrick Plasma, Ithaca, NY, USA). After taking them out from the plasma cleaner, the diced PDMS block was bonded over the PDMS membrane.
attached to the PMMA, and slowly the PDMS block-membrane combination was peeled off from the PMMA block. Thus, the substrate $S_{PM}$ was fabricated. Figure 1d shows the schematic of the $S_{PM}$ substrate. To make sure that there were no residual tensions in the membranes after bonding, the method of employing droplets as stress indicators in the membrane was employed [22]. Only membranes with a very low pre-stress value were chosen. To do this, two perpendicular diameters were drawn on the microscopic image of the droplet placed over the fabricated membrane kept horizontally. The membranes with diameter differences of less than 5% were chosen for our experiments.

For tests used to verify the accuracy of the theoretical formulation, the base-to-curing agent ratio of the membranes, PDMS coating on glass, and blocks were maintained at 10:1. The composition of the membranes used for producing the data needed for ANN modeling ranged from 5:1 to 33:1. A micrometer was used to measure the thickness of the PDMS layers that were applied to the glass substrates, and an Olympus CKX53 microscope coupled with DP74 camera was used to measure the thickness of the membrane (figure 3b).

**2.2 Experimental Setup and Methodology**

Figure 2 shows the schematic of the experimental setup. The substrate was placed on the inclined platform with the specified inclination angle $\alpha$. First, a single droplet of 1 $\mu l$ volume was placed on a surface, and its evaporation time was recorded. This was done to make sure that there was not much of a change in volume during experiments. The studies were conducted under circumstances where the droplet's evaporation duration was at least thrice as long as the times needed to collect all the necessary readings. Then, the droplets of known volume were placed onto the inclined surface with the help of variable volume micro-pipettes (Tarsons, T10, and T100) (figure 2). These micropipettes have ranges of $0 – 10 \mu l$ and $6 – 100 \mu l$ respectively. Further, the top view and side view of the placed droplets were captured using the Dino-Lite Edge 3.0 AM73915 digital microscopes to examine the onset of the droplet motion. Later, the captured images were analyzed using DinoCapture 2.0 software. As illustrated in Figures 3a and 3c, two sets of images were taken. The droplet contour images were captured from a direction normal to the plane of the inclined surface, and the contact angle images were captured by maintaining the digital microscope in the plane of the inclined surface. Multiple photos of each reading of the contact angles were captured to get an average value. A schematic of a droplet placed over an inclined substrate is shown in figure 2. Figure 3a and 3c show the top view and the side view of the droplets. As clearly visible from the top view, the droplet contour is best modeled while considering it a combination of segments of two distinct ellipses with a common minor axis. This is the inspiration for the theoretical modeling of droplet contour and the retention dynamics, which is explained in detail in the next section.

To determine the maximum retention force a substrate can apply to the droplets, the following procedure was used. At the same inclination angle, the volume of the droplet was increased step by step with the minimum step count possible in the range of $0.5 – 2 \mu L$. A droplet starts moving when the gravitational force acting on the droplet surpasses the retention or, adhesion force applied by the substrate. So, the volume of the droplet at the exact onset of motion was recorded, which was considered to be the maximum volume of droplet a substrate can retain for the given inclination angle and substrate-liquid combination.
Figure 2. Schematic of the experimental setup used in the experiments

Figure 3. Experimental pictures of a) the top view of a droplet resting on an inclined substrate along with the contours of the constituting ellipses, b) the thickness of the PDMS membrane as seen through the microscope, and c) a side view of a droplet resting on an inclined membrane, $\alpha=30^\circ$, image is rotated to make it horizontal for better visualization

3. Theoretical Model

3.1 Defining Substrate Compliance ($C_s$)

The substrate compliance depends on both the substrate and the droplet. A droplet of a larger volume can cause more deformation in a thin membrane compared to a smaller droplet. Similarly, a thinner membrane is deformed more compared to a thicker membrane of
the same Young’s modulus. Hence, in this work, a substrate compliance ($C_s$) is being defined which accounts for both the droplet and membrane characteristics. The substrate compliance is defined as follows:

$$C_s = \frac{\gamma Pt + \rho V gt}{F}$$

Here, $\gamma$ is the surface tension between air and droplet, $P$ is the droplet contour perimeter, $t$ is the thickness of the membrane, $\rho$ is the droplet density, $V$ is the droplet volume, $g$ is the acceleration due to gravity and $F$ is the flexural rigidity of the membrane defined as [40]:

$$F = \frac{Et^3}{12(1-\nu^2)}$$

Where $E$ is Young’s modulus of the membrane, $t$ is the membrane thickness and $\nu$ is Poisson’s ratio.

$C_s$ can act as the parameter representing the degree of compliance of the substrate $S_{PM}$. Higher value of $C_s$ denotes that the surface tension force combined with gravity is surpassing the force due to the flexural rigidity of the membrane ($S_{PM}$), which allows more deformation/bulge in the membrane. Similarly, a smaller value of $C_s$ denotes a smaller bulge in the thin membrane substrate $S_{PM}$. For rigid substrates, $C_s$ would be close to zero such as for substrates $S_{PLG}$ & $S_{PMMA}$. Whereas, for substrate $S_{PM}$, $C_s$ is a finite number.

### 3.2 Droplet Retention Force Model

Droplets were observed at the onset of their motion on inclined substrates. The schematic of the side view of the droplets along with all the parameters including forces are shown for compliant (figure 4a) and non-compliant (figure 4b) substrates. Here, compliant substrate represents the $S_{PM}$, and non-compliant represents $S_{PMMA}, S_{PLG}$ & $S_{PB}$. The schematic of the top view is shown in figure 4c. At the onset of sliding the gravity force is balanced by the retentive force originating from the surface tension. This value of retentive force is the maximum value of resisting force that tries to stop the droplet motion for that particular liquid-solid combination and inclination angle.

![Figure 4](https://ssrn.com/abstract=4379401)

**Figure 4.** Force balance on drops on an inclined a) compliant and b) non-compliant substrate. c) Top view of the droplets on an inclined substrate

As per the microscopic image shown in figure 3a, it is visible that the droplet contour is not in the form of a single ellipse, but a combination of two distinct ellipses with a common minor axis. This observation has also been reported by ElSherbini et al. (2004). However, the droplet contour over the inclined rigid substrates has been approximated with a single ellipse by El Sherbini and co-workers due to the complexity of modeling with two ellipses [23]. In the current work, the droplet contour is assumed to be axisymmetric with respect to Y-axis and modeled as a combination of segments of two ellipses having a common minor axis as shown.
Due to the axisymmetry of the droplet, we have
simplification can be made in the integral by using an equivalent circular radius of the ellipse. The Ramanujan’s equivalent radius
Equation 6 can be solved numerically to get the actual retentive force on the droplet. However, to solve it analytically, another
simplification can be made in the integral by using an equivalent circular radius of the ellipse. The Ramanujan’s equivalent radius

\[ \phi = \frac{\pi}{2} \]

Similarly, for ellipse 1 we get the following

\[ \cos \theta_{ellipse1} = -\frac{2}{\pi^2}H\phi^2 + \frac{4}{\pi}H\phi - 2H + \cos \theta_{Rec} \]  

Here, \( H \) is the hysteresis and is given by \( H = (\cos \theta_{Rec} - \cos \theta_{Adv}) \). Now the total retention force will be the sum of the retention force originating from the advancing side (ellipse-1) as well as the receding side (ellipse-2) of the droplet.

Net retentive force in the Y direction coming from the two ellipses is given as:

\[ F_{ret}(Retentive \ Force) = -2\gamma_l(\int_{\phi=0}^{\phi=\frac{\pi}{2}} \zeta_2(\phi)\cos \theta_1(\phi)\cos \phi d\phi + \int_{\phi=\frac{\pi}{2}}^{\phi=\pi} \zeta_1(\phi)\cos \theta_1(\phi)\cos \phi d\phi) \]  

Here, \( \zeta_1(\phi) \) is the distance of the small arc element from the center of the ellipse (figure 4c). Here, \( \gamma_l \) represents the interfacial tension between two phases, and \( \cos \theta_1(\phi) \) values need to be put accordingly. The net surface tension force is the vector sum of its components, \( F_{x1}, F_{x2} \) and \( F_{x3} \) originating from interfacial tensions \( \gamma_{1a}, \gamma_{ax}, \gamma_{ls} \) respectively. The contribution of all three interfacial tensions needs to be calculated separately and added to get the net retentive force experienced by the droplet.

Equation 6 can be solved numerically to get the actual retentive force on the droplet. However, to solve it analytically, another
simplification can be made in the integral by using an equivalent circular radius of the ellipse. The Ramanujan’s equivalent radius

\[ \zeta(\phi) = \frac{L_i}{\sqrt{\cos^2 \phi + \beta_i^2 \sin^2 \phi}} \]  

where \( L_i \) is the length of the major axis of the ellipse and, \( \beta_i = L_i/l_i \) is the aspect ratio for the ellipse, with \( l_i \) being the minor axis of the ellipse. Here, \( \phi \) refers to the azimuthal angle of the ellipse as shown in Figures 3a and 4c. Since the drop is considered
axisymmetric, the components of surface tension force along the X-axis are canceled out. Hence, the net retentive force opposing the
droplet motion is the result of the components of surface tension force acting along the contour of the droplet in the Y direction.
represents the radius of a circle with the same perimeter as that of the given ellipse [24]. The equivalent radius for an ellipse is given by:

\[
r = 0.5\{ (m + n) + 3(m - n)^2 / (10(m + n) + \sqrt{m^2 + 14mn + n^2}) \}
\] (7)

Here \(m, n\) are the length of the ellipse's semi-major and semi-minor axis respectively. Hence, we get the value of \(r_1\) for ellipses 1 and \(r_2\) for ellipse 2.

The method of integration by putting the values of equivalent radii in equation 6 is described in the Appendix. After putting the values of equivalent radii of the two ellipses and integrating the contribution of all the three interfacial tensions, we get the net retentive force as:

\[
F_s = -2\gamma_{la}r_1\left[H_{la}\left(-\frac{4}{\pi^2} + 0.5\right) - \cos\theta_R\right] - 2\gamma_{la}r_2\left[H_{la}\left(0.5 - \frac{4}{\pi^2}\right) + \cos\theta_A\right]
= \left[-2\gamma_{la}r_1\left[H_{la}k_R\left(-\frac{4}{\pi^2} + 0.5\right) - \cos\theta_R\right] + 2\gamma_{la}r_2\left[H_{la}\left(0.5 - \frac{4}{\pi^2}\right) + \cos\theta_A\right]\right] - 2\gamma_{as}(r_2 - r_1)
\] (8)

Here, a correction factor called the droplet contour factor \((k_R)\) has been introduced in equation 8 to account for the slight deviations in the shape of the droplet contour from the elliptical shape at the receding side of the drop as visible in figure 3a. The value of the drop contour factor is found iteratively to be \(-0.2\) to achieve the best match between experimental data and theoretical prediction.

Similarly, a membrane correction factor \(k_m\) is introduced to account for the resistance to stretching due to membrane elasticity. The membrane stretching factor comes out to be 0.2 for the PDMS membranes used in these experiments.

Incorporating \(k_R\) and \(k_m\) into equation 8, we get the following expression:

\[
F_s = -2\gamma_{la}r_1\left[H_{la}k_R\left(-\frac{4}{\pi^2} + 0.5\right) - \cos\theta_R\right] - 2\gamma_{la}r_2\left[H_{la}\left(0.5 - \frac{4}{\pi^2}\right) + \cos\theta_A\right] - k_M
\left[2\gamma_{la}r_1\left[H_{la}k_R\left(-\frac{4}{\pi^2} + 0.5\right) - \cos\theta_R\right] + 2\gamma_{la}r_2\left[H_{la}\left(0.5 - \frac{4}{\pi^2}\right) + \cos\theta_A\right]\right] - 2\gamma_{as}(r_2 - r_1)
\] (9)

### 3.2 Artificial Neural Network (ANN) Model

An Artificial Neural Network is a mathematical tool consisting of highly interconnected processing elements, called neurons. These neurons are further organized into 3 different layers, named input, hidden, and output layers as shown in figure 5a. Each neuron of the input and output layer is associated with one input or output variable respectively. There is no such exclusive connection between the neurons of hidden layers to the input and output variables. The hidden layer can have more than one layer, and the no. of neurons in this layer is flexible. The basic neural cell model is shown in figure 5b.

**Figure 5a** Architecture of the artificial neural network (ANN) used in the study and, b) mathematical model of an artificial neuron.
Strong interconnections exist between neurons through which data transfer happens. This data transfer is manipulated by weights and biases associated with the neurons [25]. Neural inputs include data obtained either from a user or from the previous layer of neurons. The inputs are multiplied by the corresponding weights of the connections \( w_i \), where \( i \) represents the connection from the previous neuron (see figure 5b). The weighted inputs are then summed together along with a bias giving an output of the neuron as \( s = \sum w_i x_i + b \). The output thus generated is then passed through an activation function to ensure that it stays within the activation range (between 0 and 1). The sigmoid function is one of the most commonly used activation functions in research because it may combine linear, curved, and constant behaviors [26, 27]. The output then becomes the input for the neurons of the next layers, or in the case of output layer neurons, it becomes the final result of the ANN. The final output of the network is compared to the experimentally known outputs to calculate the errors. The error is propagated backward to readjust the weights of each neuron. This process of readjusting the parameters of the network to minimize the error is known as training of the network. Selecting and training a particular ANN for any purpose includes the choice of the architecture of the network, training algorithms, and parameters used in the training of the network. Choosing the number of neurons in the hidden layer is a very important step in the training of the network and it depends on the type of experiments and also on the user’s experience. If the architecture of the model is too simple, the trained network might not have sufficient ability to learn the process correctly. Conversely, if the architecture is too complex, it may not converge during training or the trained data may be overfitted [28]. Since these types of networks learn from examples and rely on detecting the patterns in the data, there is no need to specify the relationships between various input parameters. Thus, an ANN is capable of accurately predicting unknown parameters without the need of identifying the theory behind a particular phenomenon. This feature is very helpful for modeling problems where the relationships between inputs and outputs are not clear enough or the solutions are not easily formulated in a short time [27].

**ANN architecture and Learning procedure**

Various drop and membrane parameters data were collected from the experiments. MATLAB was used to train and test the neural network. The input data included 49 experimental results or patterns corresponding to 49 specific sets for 9 input variables each. Input variables to the network include \((a, \theta_A, \theta_R, \theta_n, L, l, V) \) (volume of the retained droplet), and \( t \) (membrane thickness). Please refer to figure 4 for all the notations. The target of the network was to predict the composition (ratio of elastomer to curing agent w/w) of the given PDMS membrane. A correlation test was conducted on the input dataset to determine the dependence of different input variables of these patterns and to see whether any input variable can be omitted from the dataset. The results showed no direct dependence between any two input variables and hence no variable was excluded from the dataset. The data were divided into the training set and validation set randomly, where 80% of the data was put in the training set, and the remaining 20% was used for validation of the trained network. To pick the best possible number of neurons, testing was done on many neurons and the results were compared. To compare the performance of various architectures, there was a need to quantify the generalization capability of the network. For this purpose, root mean squared error (RMSE) along with the correlation coefficient \( (R) \) values were used, which are defined as follows:

\[
R = \frac{\sum (x - x_m)(y - y_m)}{\sqrt{\sum (x - x_m)^2 \sum (y - y_m)^2}} 
\]

\[
RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (d_i - o_i)^2} 
\]

where \( x \) and \( y \) are the sample variables being analyzed; \( x_m \) and \( y_m \) are the means of these sample variables, while \( d_i \) is the desired value, \( o_i \) are the predicted output value and \( n \) is the total number of entries [27]. The Levenberg-Marquardt back propagation (trainlm) algorithm was used for training purposes. The use and benefits of Levenberg-Marquardt to neural network training are described in previous studies [29-30]. The LM training technique is well-known for solving moderately large feed-forward neural network fitting issues quickly (up to several hundred weights). Because the solution of the matrix problem is a built-in function in the MATLAB program, the benefits of this technique are amplified [31]. During the training, the input values were normalized between 0 to 1 for computational convenience. The maximum number of iterations during the training process was taken as 1000 and the training was stopped only when either the iterations reached 1000 or the mean squared error minimum was attained, which is denoted as \( MSE = \frac{1}{n} \sum_{i=1}^{n} (d_i - o_i)^2 \). Comparison between different neural network architectures was based on the RMSE values of prediction.
4. Results and Discussion

4.1 Role of contact angles in droplet retention

Liquid-vapor, solid-vapor, and solid-liquid are the three operative surface tensions that can be defined at any point along the contact line of a droplet resting on a surface. These superficial tensions exist on the contact line lie in a plane that is at that point parallel to both the substrate and the drop contact line. Young or Neumann’s equations [41] are used to demonstrate how the projections of these three surface tensions in the direction parallel to the substrate are balanced at any location along the contact line in an equilibrium state.

The component of surface tension force parallel to the substrate is the force of resistance or adhesion (figure 6b). The surface tension force parallel to the substrate is balanced when the droplet is symmetrical with a consistent contact angle at all points along the contact line. Because of this, the drop adhesion force must be zero from a mechanical perspective (i.e., the net sum of these surface tensions over the contact line).

However, a net unbalanced surface tension force may occur over the contact line if the contact angles of the droplets along the line change, i.e. \( \cos \theta = f(\phi) \) (figure 6a), the droplet’s axisymmetry are perturbed, or both. This occurs when the droplet is placed on a heterogeneous substrate or is subjected to an external force. For example, a droplet's contact angles across the droplet contour do not remain constant when it is placed on an inclined substrate. The contact angle is highest on the advancing side while it is lowest on the receding side. The difference between these two angles, known as the contact angle hysteresis (CAH), is crucial in determining the surface tension force that works to prevent droplet motion relative to the surface. Existing literature has shown that the summation of surface tension forces is proportional to the contact angle hysteresis [23]. However, it is not the sole cause of adhesion. Two droplets of identical contact angle hysteresis might show different values of adhesive/retention force. This can happen if the droplets are of different sizes [42]. In these circumstances, the droplet contour typically also modifies, taking on an asymmetrical form along the axis perpendicular to the droplet motion, contributing along with the CAH phenomenon.

![Figure 6](image_url) Schematic showing a) top and b) side view of a drop on a smooth surface where no external force parallel to the drop is operative on the drop

4.1a Effect of substrate compliance on contact angles and contact angle hysteresis (CAH)

As discussed above, the retention force on the droplet is influenced by contact angle hysteresis (CAH) and the droplet shape. Here in this section, the contact angles and CAH of the droplet placed over different type of substrates is investigated at the time of onset of motion. So, the contact angles, and CAH discussed in this section correspond to the maximum retention force. Fig. 7 (a-d) shows the advancing and receding contact angles for substrates of varying compliances i.e, \( S_{PM}, S_{PEG}, S_{PB}, \text{and} S_{PMMA} \) respectively. The total advancing and receding angle of droplets for non-compliant substrates are \( \theta_A \) and \( \theta_R \) while for the compliant substrates, these two angles are the sum of \( \theta_A \) and \( \theta_a \) for advancing side and, \( \theta_R \) and \( \theta_r \) for the receding side, respectively (figure 4).

As the inclination angle of the substrate changes, the advancing and receding angles change for all the substrates. For the non-compliant substrates (\( S_{PEG}, S_{PB} \) and \( S_{PMMA} \)), the advancing and receding angles both decrease with the increment in substrate inclination angle (\( \alpha \)) (see Fig. 7b-d). But, for compliant substrate \( S_{PM} \), advancing angle decreases and the receding angle increases...
with the increase in the substrate inclination angle (α) (See Fig. 7a). This can be attributed to the deformation/bulging and associated resistance against bulging of the compliant substrate which restrains the shape of the droplet in such a way that the total energy of the system minimizes at equilibrium state.

Average values of the advancing angles at three different inclination angles (30°, 45° & 60°) for the different substrates are 102.87, 94.97, 86.57, and 68.44 degrees for $S_{PM}$, $S_{PCG}$, $S_{PB}$ and $S_{PMMA}$ respectively. The average values of receding angles for $S_{PM}$, $S_{PCG}$, $S_{PB}$ and $S_{PMMA}$ substrates are 47.31, 74.62, 67.93, and 46.52 respectively. Thus, substrate $S_{PM}$ showed the highest advancing angle and the substrate $S_{PMMA}$ has the lowest receding angles. The advancing angle on compliant substrate $S_{PM}$ is ~30%, ~15% & ~8% higher than the non-compliant substrates $S_{PMMA}$, $S_{PB} & S_{PCG}$ respectively. On the other hand, the receding angle on compliant substrate $S_{PM}$ is ~36% & ~30% lower than non-compliant substrates $S_{PCG} & S_{PB}$. Thus, the advancing angle ($\theta_A$) on compliant substrate $S_{PM}$ is significantly higher than non-compliant substrates and; the receding angle ($\theta_R$) on compliant substrate $S_{PM}$ is significantly lower than non-compliant substrates. This leads to differences in the contact angle hysteresis ($CAH = \theta_A - \theta_R$) for substrates of different compliances ($S_{PM}, S_{PCG}, S_{PB}, & S_{PMMA}$). CAH on the compliant substrate is significantly higher as compared to non-compliant substrates (See Fig. 8). Figure 8(a-d) shows the variation in contact angle hysteresis (CAH) with the inclination angle (α) for substrates $S_{PM}, S_{PCG}, S_{PB}$ and $S_{PMMA}$ respectively. The inset in the plot is the microscopic experimental images corresponding to each data point. As visible, the CAH decreases with the increase in inclination angle. CAH for substrates $S_{PM}, S_{PCG}, S_{PB}, & S_{PMMA}$ at (α = 30°) are 70°, 24°, 20° & 15°. Thus, at (α = 30°), CAH on the compliant substrate is more than 200% higher than the same on non-compliant substrates. This can be attributed to the deformation/bulging and associated resistance against the bulging of the compliant substrate which restrains the shape of the droplet in such a way that the total energy of the system minimizes at the equilibrium state. CAH is important as the higher CAH implies higher hysteresis force, which helps the drops in adhering to the non-horizontal surfaces [23].
Figure 7. Variation of advancing angles and receding angles for droplets of water put on different substrates: a) $S_{PM}$, b) $S_{PCG}$, c) $S_{PB}$, and d) $S_{PMMA}$. Error bars represent the standard deviation in the measured experimental data.
Figure 8. CAH for a) water on various PDMS substrates: a) $S_{PM}$, b) $S_{PCG}$, c) $S_{PB}$ and d) $S_{PMMA}$ (images are at different scales). Error bars represent the standard deviation in the measured experimental data. Red colored arrow represents the downhill direction of the inclined substrate. Scale bars in the inset images are shown using red colored line.

4.2 Geometrical Parameters of the droplets on different substrates

Here, differences in various geometrical parameters such as total length, aspect ratio, and CAH of droplets over all the substrate types ($S_{PM}, S_{PCG}, S_{PB}, \text{& } S_{PMMA}$) are studied. For direct comparison of the geometrical parameters of the droplet, water, and aqueous glycerol (60\% glycerol in water (w/w)) droplets of 25$\mu$L volume were placed on the four substrates types inclined at an angle of 30 degrees (figure 9d). The comparison of the droplet’s contact angle hysteresis (CAH), droplet length along the y-axis, and the aspect ratio is shown in figure 9(a), (b), and (c) respectively. Fig. 9(d) shows the microscopic images of the droplets placed over various substrates. The results show that the droplet resting on the free-hanging PDMS membrane ($S_{PM}$) have the highest length (5.81±0.2 mm for water and 5.97±0.2 mm for aq. glycerol) followed by the droplets resting on the $S_{PMMA}$ (5.67±0.2 mm for water and 5.33±0.2 mm for aq. glycerol) (figure 9b). However, the droplets resting on the $S_{PM}$ are narrower, i.e. have a higher aspect ratio (1.357±0.1 and 1.475±0.1 for water and aq. glycerol respectively), compared to the droplets on the $S_{PMMA}$ (1.248±0.1 and 1.143±0.1 for water and aq. glycerol respectively) (figure 9c). This can be attributed to the fact that biaxial stresses are induced on a PDMS-free-hanging thin membrane when a droplet is placed over it. This stress, in turn, affects the shape of the droplet kept on the membrane in such a way that the total energy of the system is minimized [22]. This could also explain why the droplet placed on the ($S_{PM}$) has the highest aspect ratio among all the droplets put on different substrates (figure 9c). Thus, the shapes of the droplet placed...
are highly dependent on the substrate type and the degree of compliance, with more elongated droplets on a compliant substrate. This, in turn, affects the contact angles at the advancing and receding side and thus results into variation in contact angle hysteresis (CAH) over all the substrate types. So, the contact angle hysteresis was the highest for $S_{PM}$ (32.97 degrees for water and 40.04 degrees for aq. glycerol), compared to the other two substrates ($S_{PB}$ and $S_{PCG}$) (figure 9a).

![Figure 9](image-url)

**Figure 9.** A comparison of various droplet geometric parameters: a) CAH, b) total length, and c) aspect ratio for four types of substrates. The droplets are of volume 25 μl and the inclination of the substrates was fixed at 30 degrees. Error bars represent the highest standard deviation in the recorded data (+6 degrees in 9a, ±0.2 in 9b, and around ±0.1 in 9c). d) Experimental images of droplets over various substrates as observed from the microscope camera.

### 4.3 Maximum retention force over compliant and non-compliant Substrate: validation of the theoretical model

As discussed in the previous section, the advancing and receding contact angles are influenced by the inclination angle and the substrate type (with varying compliances). They are not the same for an inclined substrate. This difference in the contact angle at advancing and receding sides i.e, the contact angle hysteresis (CAH) results in a net force applied over the droplet by the substrate due to surface tension, called net retentive force ($F_s$) (refer to section 4.1 for the schematic of forces). The droplet placed over the inclined substrate remains static until the retention force balances the net body force (gravity in the current case) applied to the droplet. With...
the increase in the inclination angle of a substrate, the net gravity force applied tangentially on the droplet along the substrate surface increases. When this gravity force surpasses the net retentive force over the droplet, it starts moving along the surface. Hence, to find out the maximum retentive force $F_s$ faced by a droplet over an inclined substrate, the droplet volume at the onset of motion was measured/recorded. The maximum retention force ($F_s$) on the droplets was measured through their retained volume ($V$) as $V = \frac{F_s}{\rho \cdot g \cdot \sin(\alpha)}$, where $\rho$ and $\alpha$ are the density of the liquid and the inclination angle of the substrate. Figure 10 (a) and (b) show the experimental and theoretical results of the volume of retained water droplets over substrates $S_{PCG}$ and $S_{PM}$ respectively at various inclination angles and thicknesses. For various inclination angles ($\alpha = 30^\circ, 45^\circ & 60^\circ$), and substrate types, the retained volume varied from $5\mu L$ to $96\mu L$. The results showed that for any given inclination, the substrate $S_{PM}$ was able to retain droplets of higher volume of water than substrate $S_{PCG}$ with comparable thickness of PDMS coating (figure 10a, b). On average, excess droplet volume is retained over $S_{PM}$ was found to be $63.33\mu L$, $47\mu L$ and $19\mu L$ at inclination angles of $30^\circ$, $45^\circ$ and $60^\circ$ degrees as compared to the substrate $S_{PCG}$ with same thickness of PDMS coatings and inclination angles. Thus, $S_{PM}$ could retain approximately $\sim 146 - 276\%$ higher droplet volumes compared to $S_{PCG}$. A comparison of data in figure 10a and 10b show that the excess volume of water droplet retained over $S_{PM}$ as compared to $S_{PCG}$ was more pronounced at lower inclination angles, compared to higher inclination angles.

Further, as visible in figure 10, the predictions from the developed theoretical model matched well with the experimental data. The maximum absolute error between the volumes of droplets predicted from our theoretical model and the experimental values is found to be $9.81\%$. Thus, the model is validated for water droplets placed over $S_{PM}$ and $S_{PCG}$ both the substrates.

4.4 Effect of substrate compliance over the droplet retention force

Here, the effect of substrate compliance ($C_S$) over the maximum retention force ($F_s$) experienced by the droplet is investigated. Free-hanging thin PDMS membrane Substrate $S_{PM}$ was used for this purpose. Membranes of thicknesses varying from 20 to $700\mu m$ inclined at an angle of $30^\circ$ were tested for their maximum retentive force. Figure 11 shows the variation in maximum retained droplet volume with the increase in substrate compliance ($C_S$). As the substrate compliance ($C_S$) increases, the volume retained increases and stagnates after a certain limit. The phenomena of increase in retained droplet volume with increment in ($C_S$) can be attributed to the fact that substrates with higher compliance values deform more which increases the contact angle hysteresis (CAH) and ultimately increases the net retentive force on the droplet. Further, the stagnation of retention force can be because of stagnation in the amount of bulge/deformation in compliant membrane beyond a level of applied force as also reported in earlier literature [43]. The developed theoretical model was able to capture this variation satisfactorily and predictions matched well with the experimental data with a maximum deviation of $9.35\%$.

4.5 Effect of substrate thickness on droplet perimeter
To observe the effect of substrate thickness on droplet perimeter at different inclinations, graphs are plotted between the perimeter of the droplet calculated and the ratio of flexural rigidity of the droplet to the thickness of the droplet (figure 12a). It was found that for the given range, the perimeter of the droplet retained is negatively correlated to the inclination angle. On average the droplet perimeter on $S_{PM}$ was 36.8 mm at 30 degrees, 29.7 mm at 45 degrees, and 23.4 mm at 60 degrees. The average perimeter shows a direct correlation with the droplet volume retained on the substrates which are, on average 92, 64, and 31.7 $\mu$l respectively, for the same inclination. This again reiterates the fact that droplet contour also plays an important role in determining the droplet retention force, in addition to CAH.

**Figure 11.** The volume of water droplet retained at an inclination of 30 degrees for membranes with different C$_s$ values. Error bars represent the highest standard deviation in the measured experimental data ($\pm2.5\ \mu$l).

**Figure 12** a) Perimeter vs (Flexural Rigidity/thickness) of the membrane b) Experimental and theoretical volume of the retained droplet on different substrates at different inclinations. The thickness of $S_{PM}$ and $S_{PCG}$ used here are 72 and 70 $\mu$m respectively. Error bars represent the highest standard deviation in the measured/recorded data (±1 mm in 12a and ±2.5 $\mu$l for $S_{PMMA}$ and $S_{PB}$ and ±2 $\mu$l for $S_{PCG}$ and $S_{PM}$ in 12b).
4.6 Comparison of droplet retention for different substrates: validation of the theoretical model

To check the validity of the given theoretical model, the model was also tested for water drops placed on $S_{PM}$, $S_{PCG}$, $S_{PMM}$ and $S_{PB}$ for 3 inclination values: 30º, 45º, and 60 degrees, and the results are plotted in figure 12(b). It was observed from the experiments that the $S_{PM}$ of thickness 72 µm was able to retain 90, 68, and 36 µl of water at an inclination angle of 30º, 45º & 60º respectively. Compared to this, $S_{PCG}$ with similar PDMS coating thickness (70µm), was able to retain 29, 17, and 13 µl of water respectively. The $S_{PMM}$ retained 25, 19, and 13 µl of a water droplet, whereas $S_{PB}$ could retain water droplets of 27, 14 and 11 µl respectively at 30, 45- and 60-degree inclination angles respectively. Thus, a compliant substrate could retain droplets of more than 200 % higher volume than other non-compliant substrates. The developed theoretical model was also able to predict the values of retained volume of droplets for these four substrates satisfactorily, with a maximum mismatch of 11.52% between the experimental values and theoretical prediction of the volume of the droplets.

4.7 Effect of liquid property over retention volume: testing the theoretical model prediction for aqueous glycerol droplets

For the $S_{PM}$ and $S_{PCG}$ substrates, a comparison is also done on the retention force offered to the water droplets and the aq. glycerol (60% w/w) droplets at an inclination of 60 degrees. It was found that on average, $S_{PM}$ were able to retain 31.67µL of water and 18.67µL of aq. glycerol (figure 13b for the given range). Similarly, $S_{PCG}$ were able to retain, on average, 12.67µL of water and 10µL of aq. glycerol solution for this range (figure 13a). Again, the $S_{PM}$ were found to retain a higher volume of liquid compared to the $S_{PCG}$ of similar thickness. Also, for the given values, the maximum absolute error between the volumes predicted by the theoretical model and experimental values was coming out to be 9.81%.

Figure 13. Comparison of experimental and theoretical values of volume of water and aq. glycerol droplet retained at 60 Degrees inclined a) $S_{PCG}$ and b) $S_{PM}$.

4.8 ANN predictions for Membrane’s Mechanical Properties

In this section, the developed ANN model is presented which is used to predict the mechanical property of the membrane by taking input from droplet retention and bulge (Table 1). Different architectures were trained and tested for the predictions. A total of 500 network architectures were tested to find the architecture that gives the best predictions for the dataset. For a single hidden layer network, the number of neurons in the hidden layer were varied from 1 to 50. Along with this, 450 networks were also tested that had double hidden layers. The number of neurons in the first hidden layers were varied from 1 to 9 while the number of neurons in the second hidden layer were varied from 1 to 50. Figure 14 shows a section of comparison of various networks of architecture 9-7-i-1, where the no. of neurons in the second hidden layer, i, is varied from 1 to 50. The root mean square of the predictions obtained in the validation steps was used to select the network which gives the best predictions. The comparison revealed that the network with architecture 9-7-8-1 generated the best predictions for the composition of the membranes. The RMSE of the training step was found to
be 3.602, while for the validation step, it was 3.588. The overall coefficient of regression comes out to be 0.90 for the network, thus indicating a good match of the predictions with the experimental data.

![RMSE of 9-7-i-1 Networks](image)

**Figure 14** Testing results of different ANN architectures (9-7-i-1), where i = (1, 50)

The ANN trained with the 80% of total experimental data points (49 nos.) converged at an epoch of 7 (figure 15a) and was able to predict the composition (weight ratio of base elastomer to curing agent) of the membrane with an overall coefficient of correlation, $R^2 = 0.90$ (figure 15b). The details of the neural network are given in Table 1. For this study the membrane thickness ranged from 20 to 50 μm, to limit the change of compliance of the membrane on droplet retention. For PDMS substrates, the membrane composition is directly responsible for the mechanical properties of the membrane.

![Convergence of the neural network](image)

**Figure 15.** a) Convergence of the neural network employed and b) Comparison of membrane composition during training and validation steps in the neural network.
be attributed to the fact that biaxial stresses are induced on a Polydimethylsiloxane (PDMS)-free-hanging thin membrane when a constant. The total length of the droplet was found to be the highest for free-hanging thin PDMS membrane substrate. Later, the effect of substrate compliance over the droplet shape was investigated keeping droplet volume and inclination angle such a way that the total energy of the system minimizes at an equilibrium state.

An analytical model is developed to determine the maximum retention force applied over the droplet by substrates of varying retentive/adhesive force applied over the droplet by a substrate (of varying degrees of compliance). ‘Poly (methyl methacrylate) (S\textsubscript{PMMA})’ and ‘Polydimethylsiloxane (PDMS) coated glass (S\textsubscript{PCG})’ surface was used as a model for rigid substrates. Whereas, ‘PDMS block (S\textsubscript{PB})’ and ‘free hanging thin PDMS membrane (S\textsubscript{PM})’ were used as a model for soft non-compliant and, soft compliant substrates. We have defined a non-dimensional number called “Substrate Compliance (C\textsubscript{S}) as C\textsubscript{S} = \frac{γPt + ρVġ}{F}, which can act as the parameter representing the degree of compliance of the substrate. Here, γ is the surface tension between air and droplet, P is the droplet contour perimeter, t is the thickness of the membrane/substrate, ρ is the droplet density, V is the droplet volume, g is the acceleration due to gravity and, F is the flexural rigidity of the membrane/substrate. Thus, C\textsubscript{S} can act as the parameter representing the degree of compliance of the substrate S\textsubscript{PM}. Higher value of C\textsubscript{S} denotes that the surface tension force combined with gravity is surpassing the force due to the flexural rigidity of the membrane (S\textsubscript{PCG}), which allows more deformation/bulge in the membrane. Similarly, a smaller value of C\textsubscript{S} denotes a smaller bulge in the thin membrane substrate S\textsubscript{PM}. For rigid substrates, C\textsubscript{S} would be close to zero such as for substrates S\textsubscript{PCG} & S\textsubscript{PMMA}. Whereas, for C\textsubscript{S} is a finite number for the substrate S\textsubscript{PM}.

An analytical model is developed to determine the maximum retention force applied over the droplet by substrates of varying compliances (ranging from a rigid substrate having zero compliance to a soft compliant membrane with significantly higher compliance). Unlike previous works in literature, here the developed model considered the contour of a droplet resting over an inclined substrate as a combination of two distinct ellipses. The developed model was able to predict the retention force offered by all the substrates (with distinct compliances, 0 < C\textsubscript{S} < 12000) satisfactorily with a maximum deviation of 11.52% from experimental results. Analysis of contact angles of a droplet at the onset of motion provided the following insights. Substrate CAH on the compliant substrate is found to be higher than the non-compliant substrates S\textsubscript{PM}, S\textsubscript{PB} & S\textsubscript{PCG} respectively. On the other hand, the receding angle on compliant substrate S\textsubscript{PM} was ~ 30%, ~15% & ~8% higher than the non-compliant substrates S\textsubscript{PMMA}, S\textsubscript{PB} & S\textsubscript{PCG} respectively. On the other hand, the receding angle on compliant substrate S\textsubscript{PM} was ~ 36% & ~30% lower than non-compliant substrates S\textsubscript{PCG} & S\textsubscript{PB}. Thus, the advancing angle (θ\textsubscript{A}) on compliant substrate S\textsubscript{PM} is found to be significantly higher than non-compliant substrates and; the receding angle (θ\textsubscript{R}) on compliant substrate S\textsubscript{PM} is significantly lower than non-compliant substrates. This led to differences in the contact angle hysteresis (CAH = θ\textsubscript{A} – θ\textsubscript{R}) for substrates of different compliances (S\textsubscript{PM}, S\textsubscript{PCG}, S\textsubscript{PB}, & S\textsubscript{PMMA}). CAH on the compliant substrate is found to be significantly higher (≥ 200% at α = 30°) as compared to non-compliant substrates. This can be attributed to the deformation/bulging and associated resistance against the bulging of the compliant substrate which restrains the shape of the droplet in such a way that the total energy of the system minimizes at an equilibrium state.

Later, the effect of substrate compliance over the droplet shape was investigated keeping droplet volume and inclination angle constant. The total length of the droplet was found to be the highest for free-hanging thin PDMS membrane substrate (S\textsubscript{PM}) among all the four-substrate tested in the current work. Similar behavior was observed for both water and aq. glycerol. It was found that droplets resting on S\textsubscript{PM} were the most elongated and, had the highest aspect ratio of around 1.47 for aq. glycerol and 1.36 for water. This can be attributed to the fact that biaxial stresses are induced on a Polydimethylsiloxane (PDMS)-free-hanging thin membrane when a

### Table 1. Details of the selected ANN

| Details of the Artificial Neural Network used in the study | |
|---|---|---|
| Network used | 9-7-8-1 | Learning Function | Gradient Descent with momentum weight and bias |
| Input Variables | \(θ\textsubscript{A}, θ\textsubscript{R}, θ\textsubscript{A}, l, t, α, V\) | Performance function | Mean Squared Error (MSE) |
| Output Variables | Membrane Composition | Transfer Function (HL) | Hyperbolic tangent sigmoid |
| Data Division | Random | Transfer Function (Output Layer) | Linear Transfer |
| Training Function | Levenberg Marquardt | Max no. of Epochs | 1000 |

### Conclusions

This paper presented a detailed investigation of the effect of substrate compliance over contact angles and maximum retentive/adhesive force applied over the droplet by a substrate (of varying degrees of compliance). ‘Poly (methyl methacrylate) (S\textsubscript{PMMA})’ and ‘Polydimethylsiloxane (PDMS) coated glass (S\textsubscript{PCG})’ surface was used as a model for rigid substrates. Whereas, ‘PDMS block (S\textsubscript{PB})’ and ‘free hanging thin PDMS membrane (S\textsubscript{PM})’ were used as a model for soft non-compliant and, soft compliant substrates. We have defined a non-dimensional number called “Substrate Compliance (C\textsubscript{S}) as C\textsubscript{S} = \frac{γPt + ρVġ}{F}, which can act as the parameter representing the degree of compliance of the substrate. Here, γ is the surface tension between air and droplet, P is the droplet contour perimeter, t is the thickness of the membrane/substrate, ρ is the droplet density, V is the droplet volume, g is the acceleration due to gravity and, F is the flexural rigidity of the membrane/substrate. Thus, C\textsubscript{S} can act as the parameter representing the degree of compliance of the substrate S\textsubscript{PM}. Higher value of C\textsubscript{S} denotes that the surface tension force combined with gravity is surpassing the force due to the flexural rigidity of the membrane (S\textsubscript{PCG}), which allows more deformation/bulge in the membrane. Similarly, a smaller value of C\textsubscript{S} denotes a smaller bulge in the thin membrane substrate S\textsubscript{PM}. For rigid substrates, C\textsubscript{S} would be close to zero such as for substrates S\textsubscript{PCG} & S\textsubscript{PMMA}. Whereas, for C\textsubscript{S} is a finite number for the substrate S\textsubscript{PM}.

An analytical model is developed to determine the maximum retention force applied over the droplet by substrates of varying compliances (ranging from a rigid substrate having zero compliance to a soft compliant membrane with significantly higher compliance). Unlike previous works in literature, here the developed model considered the contour of a droplet resting over an inclined substrate as a combination of two distinct ellipses. The developed model was able to predict the retention force offered by all the substrates (with distinct compliances, 0 < C\textsubscript{S} < 12000) satisfactorily with a maximum deviation of 11.52% from experimental results. Analysis of contact angles of a droplet at the onset of motion provided the following insights. Substrate CAH on the compliant substrate is found to be higher than the non-compliant substrates S\textsubscript{PM}, S\textsubscript{PB} & S\textsubscript{PCG} respectively. On the other hand, the receding angle on compliant substrate S\textsubscript{PM} was ~ 30%, ~15% & ~8% higher than the non-compliant substrates S\textsubscript{PMMA}, S\textsubscript{PB} & S\textsubscript{PCG} respectively. On the other hand, the receding angle on compliant substrate S\textsubscript{PM} was ~ 36% & ~30% lower than non-compliant substrates S\textsubscript{PCG} & S\textsubscript{PB}. Thus, the advancing angle (θ\textsubscript{A}) on compliant substrate S\textsubscript{PM} is found to be significantly higher than non-compliant substrates and; the receding angle (θ\textsubscript{R}) on compliant substrate S\textsubscript{PM} is significantly lower than non-compliant substrates. This led to differences in the contact angle hysteresis (CAH = θ\textsubscript{A} – θ\textsubscript{R}) for substrates of different compliances (S\textsubscript{PM}, S\textsubscript{PCG}, S\textsubscript{PB}, & S\textsubscript{PMMA}). CAH on the compliant substrate is found to be significantly higher (≥ 200% at α = 30°) as compared to non-compliant substrates. This can be attributed to the deformation/bulging and associated resistance against the bulging of the compliant substrate which restrains the shape of the droplet in such a way that the total energy of the system minimizes at an equilibrium state.

Later, the effect of substrate compliance over the droplet shape was investigated keeping droplet volume and inclination angle constant. The total length of the droplet was found to be the highest for free-hanging thin PDMS membrane substrate (S\textsubscript{PM}) among all the four-substrate tested in the current work. Similar behavior was observed for both water and aq. glycerol. It was found that droplets resting on S\textsubscript{PM} were the most elongated and, had the highest aspect ratio of around 1.47 for aq. glycerol and 1.36 for water. This can be attributed to the fact that biaxial stresses are induced on a Polydimethylsiloxane (PDMS)-free-hanging thin membrane when a
A droplet is placed over it. This stress, in turn, affects the shape of the droplet kept on the membrane in such a way that the total energy of the system is minimized.

Further, the study highlighted the difference in retention force offered by compliant and non-compliant substrates having similar surface characteristics. It was found that substrate $S_{PM}$ could retain approximately $\sim 146 - 276 \%$ higher droplet volumes compared to $S_{PEG}$. A similar trend was followed by aq. glycerol droplets.

In the last section, we have developed and employed an Artificial Neural Network (ANN) model to predict the composition of any unknown Polydimethylsiloxane (PDMS) membrane by using various observable parameters from the experiments; droplet resting and onset of motion over a thin membrane substrate $S_{PM}$. The developed ANN was able to predict the membrane composition with an overall $R = 0.90$. This study provided a detailed understanding of the dynamics of droplets at the onset of motion placed over substrates of varying compliances. The methodology of fitting the droplet contact line with a combination of two ellipses is found to work well for axisymmetric droplets on both compliant and non-compliant surfaces. The study would benefit a variety of applications, such as fuel cell technologies, anti-icing, and cleaning technologies. The insights would be helpful in applications such as droplet condensation on thin membranes, films, etc.

Acknowledgments

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CRediT authorship contribution statement

Syed Ahsan Haider: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Validation; Visualization;

Writing - original draft. Rohit: Investigation; Methodology; Validation; Visualization. Abhishek Raj: Conceptualization, Funding acquisition, Resources; Supervision, Project administration; Writing – review & editing.

Declaration of competing Interest

The authors have no conflict of interest.

Data availability

The data that support the findings of this study is available from the corresponding author upon request.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>$\rho$</td>
<td>Density of the droplet</td>
<td>$[\text{kg/m}^3]$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Inclination angle of the substrate</td>
<td>$(^\circ)$</td>
</tr>
<tr>
<td>$g$</td>
<td>Acceleration due to gravity</td>
<td>$[\text{m/s}^2]$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Azimuthal angle</td>
<td>$(^\circ)$</td>
</tr>
<tr>
<td>$\theta_a$, $\theta_r$</td>
<td>Advancing and receding contact angles respectively (above drop contact curve plane)</td>
<td>$(^\circ)$</td>
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<tr>
<td>$\theta_a$, $\theta_r$</td>
<td>Advancing and receding contact angles respectively (below drop contact curve plane)</td>
<td>$(^\circ)$</td>
</tr>
</tbody>
</table>
\[
H_{la} = \cos \theta_R - \cos \theta_A
\]
\[
H_{ls} = \cos \theta_L - \cos \theta_a
\]
\[
k_R \quad \text{Droplet contour factor for receding side}
\]
\[
k_M \quad \text{Membrane factor}
\]
\[
\gamma_{la}, \gamma_{ls}, \gamma_{as} \quad \text{Interfacial tension between liquid-air and liquid-substrate, air-substrate respectively} \quad [\text{N/m}]
\]

References


Figure A1 Force balance on drops on an inclined a) compliant and b) non-compliant substrate. c) Top view of the droplets on an inclined substrate

At the onset of the motion of the droplet, two forces are coming into play. The gravity force, denoted by $F_g$, tries to cause the motion, and the surface tension force, $F_s$, responsible for retaining the droplet on the surface (figure A1). The surface tension force is further divided into three components: $F_{s1}$, $F_{s2}$, and $F_{s3}$. These three forces are coming due to the surface tension between air-liquid, air-solid, and solid-liquid respectively. On a rigid substrate, these forces follow Young’s equation, while on a compliant soft substrate; the equilibrium is governed by the Neumann law [42], as shown in figure A1.

Since the droplet is considered to be axisymmetric along the $Y$ axis (figure A1c) the surface tension components in the $X$ direction get canceled out. Hence, the resultant surface tension will be calculated in the $Y$ direction only and can be calculated using equation 6, as shown in the main text:

$$ F_{s1}(\text{Retentive Force}) = -2\gamma \left( \int_{\phi=0}^{\phi=\pi/2} \xi_2(\phi) \cos\theta_1(\phi) \cos\phi d\phi + \int_{\phi=\pi/2}^{\phi=\pi} \xi_1(\phi) \cos\theta_1(\phi) \cos\phi d\phi \right) $$  \hspace{1cm} \text{A1}$$

Since the droplet shape is constituted from two separate ellipses with a common minor axis, the integral is split into two parts with appropriate limits to:

$$ F_{s1}(\text{Retentive Force}) = -2\gamma \left( \int_{\phi=\pi/2}^{\phi=\pi} \xi_1(\phi) \cos\theta_1(\phi) \cos\phi d\phi + \int_{\phi=0}^{\phi=\pi/2} \xi_2(\phi) \cos\theta_1(\phi) \cos\phi d\phi \right) = I_1 + I_2 $$  \hspace{1cm} \text{A2}$$

Here the first term on the RHS (shown in green) is integration done for ellipse 2. Due to axisymmetry, the limits are taken only from 0 to $\pi/2$, and the entire integral is multiplied by 2 in the beginning (as shown in red). Similarly, the integration is done for ellipse 1 (shown in blue) and the same rationale is applied for axisymmetry.

We solve the integral $I_1$ as follows, i.e. for ellipse 1 (equation A1):
Using Ramanujan’s equivalent radii formula, as shown in equation 7 [24], is used to replace the azimuthal angle dependant ellipse radius \( \left( \zeta_1(\phi) \right) \) with a constant radius of an equivalent circle:

\[
-2\gamma_i \int_{\phi=\pi/2}^{\phi=\pi} \zeta_1(\phi) \cos \theta_i(\phi) \cos \phi d\phi
\]

Putting the function of \( \cos \theta_i(\phi) \) derived above for ellipse 1

\[
-2\gamma_i [ \int_{\phi=\pi/2}^{\phi=\pi} \zeta_1(\phi) \cos \theta_i(\phi) \cos \phi d\phi ] = -2\gamma_i [ \frac{1}{\pi^2} H_i \phi^2 + \frac{1}{\pi} H_i \phi + 2H_i + \cos \theta_{R1} ] \cos \phi d\phi
\]

Integrating using suitable formulae, we get:

\[
-2\gamma_i \left\{ H_i \left( -\frac{1}{\pi^2} + 0.5 \right) \cos \theta_{R1} \right\}
\]

So for ellipse 1, we have:

\[
-2\gamma_i \int_{\phi=\pi/2}^{\phi=\pi} \zeta_1(\phi) \cos \theta_i(\phi) \cos \phi d\phi = -2\gamma_i \left\{ H_i \left( -\frac{1}{\pi^2} + 0.5 \right) \cos \theta_{R1} \right\}
\]

Similarly, we solve the second integral, \( I_2 \) as follows, i.e. for ellipse 2 (equation A2):

\[
-2\gamma_i \int_{\phi=0}^{\phi=\pi/2} \zeta_2(\phi) \cos \theta_i(\phi) \cos \phi d\phi
\]

Again using Ramanujan’s equivalent radii formula, equation 7, to replace the ellipse radius with a constant radius of equivalent circle

\[
-2\gamma_i [ \int_{\phi=\pi/2}^{\phi=\pi} \zeta_2(\phi) \cos \theta_i(\phi) \cos \phi d\phi ] = -2\gamma_i [ \frac{1}{\pi^2} H_i \phi^2 + \frac{1}{\pi} H_i \phi + \cos \theta_{R2} ] \cos \phi d\phi
\]

Putting the function of \( \cos \theta_i(\phi) \) derived above for ellipse 2

\[
-2\gamma_i [ \int_{\phi=\pi/2}^{\phi=\pi} \zeta_2(\phi) \cos \theta_i(\phi) \cos \phi d\phi ] = -2\gamma_i [ \frac{1}{\pi^2} H_i \phi^2 + \cos \theta_{A1} ] \cos \phi d\phi
\]

Integrating using suitable formulae, we get:

\[
-2\gamma_i \left\{ H_i \left( 0.5 - \frac{1}{\pi^2} + \cos \theta_{A1} \right) \right\}
\]

So for ellipse 2, we have:

\[
-2\gamma_i \int_{\phi=0}^{\phi=\pi/2} \zeta_2(\phi) \cos \theta_i(\phi) \cos \phi d\phi
\]
The above-derived equations A7 and A12 are for a general case regarding ellipses 1 and 2. It can be used for calculation regarding all three surface tensions ($\gamma_{la}, \gamma_{ls}, \gamma_{as}$) at the contact lines by suitably putting the values of the contact angles at the advancing side and the receding side ($\cos\theta_A$ and $\cos\theta_R$, respectively) along with the corresponding hysteresis function, ($H_i = \cos\theta_R - \cos\theta_A$).

After doing the integration for all three surface tension forces, we have the following results:

For $F_{s1}$, we have:

$$F_s = -2\gamma_{la}r_1 \left\{ H_{la} \left( -\frac{4}{\pi^2} + 0.5 \right) \cdot \cos\theta_R \right\} - 2\gamma_{la}r_2 \left\{ H_{la} \left( 0.5 - \frac{4}{\pi^2} \right) + \cos\theta_A \right\}$$

For $F_{s2}$, we have:

$$F_s = -2\gamma_{as}(r_2 - r_1)$$

Similarly, for $F_{s3}$, we are left with:

$$F_s = -2\gamma_{la}r_1 \left\{ H_{ls}kR \left( -\frac{4}{\pi^2} + 0.5 \right) \cdot \cos\theta_r \right\} - 2\gamma_{ls}r_2 \left\{ H_{ls} \left( 0.5 - \frac{4}{\pi^2} \right) \cos\theta_a \right\}$$

After the summation of contributions of retentive force from all the 3 surface tensions, the final equation becomes:

$$F_s = -2\gamma_{la}r_1 \left\{ H_{la} \left( -\frac{4}{\pi^2} + 0.5 \right) \cdot \cos\theta_R \right\} - 2\gamma_{la}r_2 \left\{ H_{la} \left( 0.5 - \frac{4}{\pi^2} \right) + \cos\theta_A \right\}$$

$$- \left[ 2\gamma_{la}r_1 \left\{ H_{la}kR \left( -\frac{4}{\pi^2} + 0.5 \right) \cdot \cos\theta_r \right\} + 2\gamma_{ls}r_2 \left\{ H_{ls} \left( 0.5 - \frac{4}{\pi^2} \right) \cos\theta_a \right\} \right] - 2\gamma_{as}(r_2 - r_1)$$

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