DYNAMIC WETTING: HYDRODYNAMIC
OR MOLECULAR-KINETIC?

By

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ABSTRACT

The dynamic wetting behavior of simple liquids (water, glycerin, formamide, ethylene glycol, and a mixture of water and ethylene glycol) and polydimethylsiloxane (PDMS) oils with different viscosities has been investigated. The hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic models have been applied to the experimental results to evaluate each model's adequacy. The hydrodynamic model does not explain the experimentally observed dependence of dynamic contact angles on the contact velocity of simple liquids, and the fitted parameter (L_s) value is not physically reasonable; all are in the sub-atomic dimension. The molecular-kinetic model fits reasonably well with the experimental data of simple liquids, but the fitted parameters (λ and K_w) are significantly different in advancing and receding cases. Finally, for simple liquids investigated in this work, the combined molecular-hydrodynamic model is not superior when compared to the molecular-kinetic model, which contradicts the literatures. These observations lead to a conclusion that the molecular displacement (adsorption and desorption) process seems to be dominant for the simple liquids investigated in this work. However, the inconsistency in the advancing and receding cases question the assumption in the molecular-kinetic model that "the same amount of work is done on each site, irrespective of whether the adsorption site is occupied by the advancing phase or the receding phase."

For the dependence of dynamic contact angles on the contact velocity for PDMS oils, the hydrodynamic model fits well with experimental results in terms of a linear

relationship, but the fitted equilibrium contact angles are significantly different from the measured values. The molecular-kinetic model provides a relatively poor fitting to the experimental data of PDMS oils. Although the combined model fits reasonably well with the experimental data in terms of curve fitting, the fitted parameter K_w is practically less meaningful. This work provides the first, to the best of knowledge, extensive comparison of the three models with experimental data using a wide range viscosity. Remarkably, the work suggests that none of the evaluated models is sufficient to explain the dependence of dynamic contact angles of the investigated PDMS oils on contact velocity.

The contact angle hysteresis of the simple fluids and PDMS oils has also been investigated. The work supports the hypothesis that the hysteresis strongly depends on the interactions between the contacting fluids and the solid substrate and reports the dependence of hysteresis on fluid viscosity for the first time.

Chapter I

INTRODUCTION

The dynamic wetting phenomenon is important in numerous industrial and natural processes. When a fluid is displacing another immiscible fluid on a solid surface, the point at which the three phases meet is known as three phase boundary. If the three phase contact line is in continuous motion, it is called dynamic wetting. The angle between the moving contact line and solid surface is defined as the dynamic contact angle; depending upon the direction of the contact line movement, it is classified either as the advancing contact angle or as the receding contact angle.

The complete mechanism of dynamic wetting is not understood. There are three widely recognized dynamic wetting models in the literature: hydrodynamic,^{1, 2} molecular kinetic,^{3, 4} and combined molecular-hydrodynamic.⁵ The hydrodynamic model describes the dynamic wetting in terms of bulk viscous dissipation and does not take the solid surface into account, whereas the molecular kinetic model describes the dynamic wetting as a rate process of molecular “jumps” on a solid surface. The combined model is a combination of the molecular-kinetic and hydrodynamic models. There are controversies over the applicability of these theories to the dynamic wetting behavior of liquids on solid surfaces and the relationship between the models’ parameters and physicochemical properties of solids and/or liquids. Chapter II reviews the fundamentals of equilibrium and dynamic wetting and their measurements, and the theoretical models and their application to different systems in the literature. Chapter II also discusses the

controversies over the relationship between model parameters and solid/liquid properties in the literature.

The motivation for this work is to experimentally investigate the velocity dependence of advancing and receding dynamic contact angles, and then to check the applicability of the dynamic wetting models (hydrodynamic, molecular kinetic, and combined) to experimental data. In order to obtain a systematic relationship, different systems have to be investigated. In this work, a variety of simple liquids and silicone oils of different viscosities (5 cSt - 60,000 cSt) have been chosen for a systematic study. There are limited literatures available on the viscosity effect and comparison of models with viscosity data. This work aims to investigate the viscosity effect by conducting experiments using polydimethylsiloxane (PDMS) oils with different viscosities on fluoropolymer surfaces. The advantage of using PDMS oils is that the viscosity of oil can be changed without changing other properties, like surface tension and density, significantly.

Chapter III describes the materials used and the advanced methods of investigating contact angles in this study. Chapter IV describes the results obtained and the application of hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic models for each individual system. The discussion of models' parameters and contact angle hysteresis are also presented in Chapter IV. Finally, Chapter V summarizes the conclusions from the present work.

Chapter II

BACKGROUND

2.1 Wetting

The wetting of solid surfaces plays a central role in many natural and industrial processes. For example, the wetting of surfaces by paint and ink is critical for coating and printing industries;⁶ wetting of pipe lines by corrosive fluids is essential for corrosion inhibition; how well the pesticides wet the plant leaf surface is important for pesticides manufacturing industries. In addition, wetting is important in froth flotation, lubrication, and oil recovery.³

Wetting is usually quantified by contact angles. When a small drop of liquid is placed on a solid surface, it will either completely spread on the surface or may remain as a stable segment of a sphere on the surface, as shown in Figure 2.1.⁷ The contact angle θ , is the angle between the solid surface and the tangent line drawn against the droplet surface. Depending on the value of the contact angle, wetting is characterized as complete wetting (when $\theta = 0^\circ$), partial wetting (when $0^\circ < \theta < 90^\circ$), and dewetting (when $\theta \geq 90^\circ$).⁸

The point where the three phases (solid, liquid, and vapor in Figure 2.1) meet is known as the three phase boundary. Young's equation represents the relationship between contact angle and interfacial tensions:⁸

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (2.1)$$

In Equation 2.1, γ_{sv} , γ_{sl} , and γ_{lv} are the interfacial tensions of solid-vapor, solid-liquid, and liquid-vapor, respectively.

Wetting is classified into two different categories, equilibrium or static, when the three phase boundary is stationary, and dynamic, when the three phase boundary is moving. Although dynamic wetting is commonly seen in many industrial and practical processes, most of the studies involve equilibrium wetting and only a small number of studies have focused on dynamic wetting.^{9,10} In spite of its importance in numerous applications, the fundamentals of dynamic wetting are not fully understood, and there is a need to understand the complete mechanism of dynamic wetting.

2.2 Measurement of Contact Angles

2.2.1 Equilibrium Contact Angle Measurement

There are many different techniques to measure equilibrium contact angles, such as the tilting plate method, sessile drop method, and pendant drop method.⁸ The most common method to measure the equilibrium contact angle is the sessile drop method. During this experiment, a small droplet of liquid is placed on a horizontal solid surface and tangent line along the liquid drop is drawn (Figure 2.1b), to quantify the angle between the solid surface and the tangent. The detailed method of this measurement is explained in Chapter III. Contact angles may vary on a single solid surface at different sites due to the heterogeneity of the surface¹¹ and the equilibrium contact angle is the average of several consistent measurements.

2.2.2 Dynamic Contact Angle Measurement

The equilibrium contact angles are insufficient to quantify the dynamic wetting, instead, the dynamic contact angles better represent the dynamic wetting behavior of a liquid on a solid surface.¹¹ When the three phase contact line is moving in the forward direction (solid goes into the liquid), the dynamic contact angle is termed as the advancing contact angle, and when the contact line motion is in the reverse direction (solid comes out of the liquid), it is called the receding contact angle.⁶

There are two widely used techniques to experimentally measure the dynamic contact angle, the first approach is the direct visualization (optical) and second is the capillary force (Wilhelmy plate) measurement. In the case of optical measurement, a direct visualization of the moving contact line is carried out through a microscope attached to a camera. Recently, high speed CCD cameras are being used to catch the faster changes in contact angles. This technique has been applied to pure liquids as well as liquid mixtures.¹¹ The major advantage of the optical method is the convenience of using this method over a wide range of velocities. The draw back of this method is that the accuracy of the measurement is only $\pm 1^\circ$.^{6,9}

The Wilhelmy plate measurement is an indirect approach to measure dynamic contact angles. A force exerted by the liquid on the solid surface is measured through a sensitive balance, and the dynamic contact angle is calculated from this force along with known liquid surface tension and solid wetted length.⁶ The detailed procedure is explained in Chapter III. The major advantages of the Wilhelmy plate method are highly reproducible results with great sensitivity ($\pm 0.1^\circ$) and better control on the experiment.

The disadvantage of this technique is that the wetting surface must be uniform with the same surface characteristics on both sides.⁶

2.3 Velocity Dependence of Dynamic Contact Angles

Although the equilibrium contact angle is a characteristic property of a particular solid/liquid system, studies have shown that the contact angles change from their equilibrium values as functions of velocity as well as the direction of the three phase contact line movement.^{3-5,9,12,13,15-23} The advancing contact angle increases with speed whereas the receding contact angle decreases, reaching the maximum and minimum possible values of 180° and 0° respectively at high velocities.^{3,11,17} If the velocity is further increased after the advancing contact angle reaches 180° , entrainment of the air (receding phase) occurs and ultimately the three phase contact line will break down.³

Historically, there were some controversies over the method of measurement in the literature,^{24,25} but the controversies were resolved later on by conducting experiments on the same system using the Wilhelmy plate method and comparing the results with optical measurements. For example, Hayes and Ralston performed experiments on a polyethylene terephthalate (PET)/ water/ air system using the Wilhelmy plate method and observed that the advancing contact angle increased with the velocity.⁹ These results were in good agreement with optical results on the same system obtained by T.D.Blake.²⁶ When compared to optical methods, the Wilhelmy plate method gives more accurate values of contact angles even for very low speeds.⁶ If the contact angle changes slightly, it is difficult to measure the contact angle beyond the optical resolution using optical

methods, while the Wilhelmy plate method measures very small changes in force using a sensitive electronic balance.⁹ Therefore, the Wilhelmy plate method is very useful in studying the dynamic effects of wetting.

One remaining controversy is how the dynamic contact angle quantitatively changes with the velocity of the three phase contact line. Hayes and Ralston compared the results obtained by various researchers, and there is no consensus about the velocity dependence of contact angles.⁹ In most of the studies, the experiments were conducted within small ranges of velocities, and observed relationships were different, depending on the system and experimental velocity range. In order to have a better understanding of the dependence of dynamic contact angles on velocity, a broad range of velocities and different sets of systems (many liquids on the same surfaces or the same liquid on different substrates) are required.

2.4 Models of Dynamic Wetting

It is important to understand the basic controlling mechanism of the wetting process and to develop models to predict the behavior of the system beyond the experimental limitations. In the modeling of dynamic wetting, the main challenge is that “the submicroscopic length scales at which real wetting process takes place, but the typical experimental observations are made at macroscopic scales”.²⁷ There are two broad categories of dynamic wetting models in the literature: hydrodynamic^{1,2} and molecular-kinetic^{3,4}. Recently, a combined molecular-hydrodynamic⁵ model has been proposed. These three models are explained in detail in the following sections.

2.4.1 Hydrodynamic Model

Cox developed a macroscopic model which considers that the three phase contact line motion is due to viscous dissipation, assuming the bulk viscous friction is the main resistance force for three phase contact line motion.¹ This model does not take solid surface properties into account. The hydrodynamic model is developed by dividing dynamic meniscus into two regions (Figure 2.2a), an inner zone (size L_s) and an outer zone (size, L).²⁸ In the outer zone, the “no slip” boundary condition of classical hydrodynamics (viscous dissipation is the dominant force) is applied, whereas it is assumed that the slippage of fluid occurs in the inner zone close to the solid surface (the first couple of layers of molecules).^{11,17} Cox derived the generalized solution of hydrodynamic model as:¹

$$g(\theta_d) = g(\theta_o) \pm Ca \ln\left(\frac{L}{L_s}\right). \quad (2.2)$$

$g(\theta)$ is a complex integral function, but for solid/ liquid/ gas systems, it can be simplified to $\theta^3/9$,² thus the equation for hydrodynamic model becomes:

$$(\theta_d)^3 = (\theta_o)^3 \pm 9 \frac{\eta V}{\gamma_{lv}} \ln\left(\frac{L}{L_s}\right). \quad (2.3)$$

where θ_d , θ_o are dynamic and equilibrium contact angles, respectively; η is the liquid viscosity; V is the three phase contact line speed; γ_{lv} is the liquid-vapor interfacial tension; L is the capillary length; L_s is the slip length. In Equations 2.2 and 2.3, the positive sign is for the advancing movement and the negative sign corresponds to the receding movement of the contact line.

In the hydrodynamic model, $\ln\left(\frac{L}{L_s}\right)$ is considered to be a fitting parameter. The size of the outer region, L , is used as the maximum capillary length and can be calculated from $L = \sqrt{2\gamma_{lv}/\rho g}$, where ρ and g are liquid density and gravity, respectively.^{13,29} The size of the slip region, L_s , is considered to be the distance from the three phase boundary to the point where the “no-slip” boundary condition is applicable.^{17,30} Generally, the value of L_s is assumed to be 1-2 molecular layers over the surface.²⁷ The exact physical origin and boundary conditions of the slip region are unknown.^{26,27} “The slippage of fluid was introduced to avoid the stress singularity due to the application of the ‘no-slip’ boundary condition of hydrodynamics at the three phase boundary”.^{1,23} The molecular-dynamics (MD) simulation studies also support the idea of assuming the slip condition near the three phase boundary.³⁰

2.4.2 Molecular-Kinetic Model

This model is based on the Eyring’s statistical treatment of the transport process.¹⁴ Yarnold and Mason found that the contact angle changes with the displacement of molecules at the three phase boundary.¹⁵ Blake and Haynes proposed that “the three phase contact line moves only when the molecules of the receding phase (fluid 2), at the adsorption sites of the solid surface, are replaced by the molecules of the advancing phase (fluid 1)”.⁴

The movement of liquid molecules at the three phase contact line is schematically shown in Figure 2.2b. The molecular-kinetic model predicts the contact angle

dependence on contact line velocity by incorporating the microscopic properties of the solid surface. The relationship between dynamic contact angle and the velocity of the three phase contact line is³

$$\cos \theta_d = \cos \theta_o \mp \frac{2kT}{\gamma_{lv}\lambda^2} \operatorname{arcsinh}\left(\frac{V}{2K_w\lambda}\right). \quad (2.4)$$

where, k is the Boltzmann constant; T is the absolute temperature; λ is the distance between adsorption sites; V is the velocity of the contact line; and K_w is the quasi-equilibrium rate constant.

In Equation 2.4, the negative sign is for the advancing movement and the positive sign is for the receding movement of the contact line, and λ and K_w are adjustable parameters in the molecular kinetic model. According to the model, the values for λ and K_w should be in the order of molecular dimensions (1 nm) and 10^6 sec^{-1} respectively.^{13,26} In order to follow the molecular kinetic model, the experimental data should be fitted to Equation 2.4, and the values for λ and K_w must be physically reasonable.

2.4.3 Combined Molecular-Hydrodynamic Model

Recently, Petrov and Radoev combined the viscous dissipation (Cox-Voinov^{1,2}) and the molecular displacement (Blake-Haynes⁴) approaches to explain the velocity dependence of dynamic contact angle.¹⁶ During the motion of the contact line, nonhydrodynamic frictional force is dominant near the three phase boundary while the bulk viscous force is dominant away from the three phase boundary.¹¹ “The

nonhydrodynamic frictional force near the three phase contact line is related to the equilibrium and Young's contact angle as:^{2,5}

$$\cos \theta_o = \cos \theta_y \pm \frac{F(V)}{\gamma} . \quad (2.5)$$

$F(V)$ near the contact line can be defined as:^{3,5}

$$F(V) = 2nkT \operatorname{arcsinh} \left(\frac{V}{2K_w \lambda} \right) . \quad (2.6)$$

Thus, the equilibrium contact angle can be written as:

$$\theta_o(V) = \arccos \left[\cos \theta_y \mp \left(\frac{2kT}{\gamma \lambda^2} \right) \operatorname{arcsinh} \left(\frac{V}{2K_w \lambda} \right) \right] . \quad (2.7)$$

Here, θ_y will be replaced with measured equilibrium contact angle, θ_o . Petrov and Petrov inserted Equation 2.7 into the hydrodynamic equation to obtain the combined model equation as:⁵

$$(\theta_d)^3 = [\theta_o(V)]^3 \pm (9\eta V/\gamma) \ln(L/L_s) . \quad (2.8)$$

In Equations 2.7 and 2.8, K_w , λ and L_s are considered to be fitting parameters. They can be obtained by simultaneously fitting the data with Equations 2.7 and 2.8. All the constants in the combined model are the same as in the molecular kinetic and hydrodynamic models.

2.5 Comparison of Models with Experimental Results in the Literature

There are controversies over the applicability of theoretical models to experimental dynamic contact angle data and in relating the model parameters to the

solid/liquid properties. Cox¹ compared his hydrodynamic model (Equation 2.2) with experimental data of a glass/ silicone oils/ air system performed by Hoffman¹⁸ and found that the results were in good agreement with the hydrodynamic model (Equation 2.3) over the observed velocity region. Fermingier and Jenffer¹⁹ conducted experiments on glycerol, displacing the PDMS oils of different viscosities (V10, V100, and V1000) in a capillary tube. From their analysis they concluded that the hydrodynamic model only explains the dynamic wetting qualitatively, since Equation 2.3 did not fit quantitatively. R. T. Foister observed a broad range of viscosity ratios (receding fluid to advancing fluid, 5.9×10^{-3} –3180), and concluded that the hydrodynamic model fits only the data obtained for low capillary numbers ($Ca < 1$) and that the microscopic dynamics are required to establish a complete relationship between the wetting kinetics and material properties of the liquids and solids.²⁰ On the other hand, the dynamic contact angles of water on a PET surface show that the hydrodynamic model fits well with the low velocity region data (Figure 2.3), but that the model gives physically unreasonable (“smaller compared to the molecular dimensions”) values for the slip length.⁹

Blake and Haynes measured dynamic contact angles of a glass/ water/ benzene system using an optical method and developed the molecular kinetic model by taking molecular displacement at the three phase contact line into consideration.⁴ The results were in good agreement with theoretical predictions. A multi-mechanism behavior over a wide range of velocities (3.16×10^{-5} –10 m/sec) has been observed for a PET/ water / air system (Figure 2.4).²⁶ The molecular-kinetic model gives two different sets of parameters (λ , and K_w) for very high and low velocities. For intermediate velocities, non singular sets

of parameters are observed and the non-singularity is explained as a stick-slip movement of three phase contact line.²⁶ Petrov and Petrov conducted experiments on the PET/ aqueous glycerol solutions/ air system over the low velocity region (0.1-100 mm/sec) and, surprisingly, they obtained two different sets of parameters within this velocity region using the molecular-kinetic model.²¹

Figure 2.5 shows, a single curve fit of the molecular-kinetic model is enough for the entire experimental velocity range (0.6 mm/min-300 mm/min) of the advancing contact angles of water on a PET substrate.⁹ Although both studies were using the optical method, the difference between the contact angle values of Blake²⁶ and Petrov and Petrov²¹ is because the PET surface has been modified in the latter's study.⁹ Table 2.1 shows the fitted λ and K_w values from different authors.^{3,9,21} In addition, Hayes and Ralston⁹ conducted experiments on a PET/ aqueous glycerol/ air system (not shown here). From their study, they concluded that, although the molecular-kinetic model better describes the dynamic wetting behavior of water and glycerol solution with a physically reasonable single set of parameters, the viscosity effects should be considered.⁹

The dynamic contact angles of octamethylcyclotetrasiloxane (OMCTS) on low energy fluoropolymer surfaces along with the fitting of hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic models, are shown in Figure 2.6.¹³ Neither the hydrodynamic nor the molecular-kinetic model fits the data over the entire velocity range, but the combined molecular-hydrodynamic model does. The fitted parameters are shown in Table 2.2; the equilibrium contact angles from the model fittings are significantly different in the advancing and the receding cases as well as from the model

to model. Similar observations were also made for hexadecane (not shown here). Although the combined molecular-hydrodynamic model fits well with the data in the entire velocity region, the L_s values are significantly larger than the molecular dimensions of hexadecane and OMCTS. From their study, Schneemilch et al. concluded that the parameter, L_s , may not represent the molecular dimensions.¹³

The fitting of all three (hydrodynamic, molecular-kinetic, and combined) models with the dynamic wetting behavior of different simple liquids (CCl_4 , tert-butanol, and OMCTS) on fluorinated surfaces is shown in Figure 2.7.²² The hydrodynamic model fits well only with medium and high velocity data for all liquids (Figure 2.7a), but the slip length, L_s , value for CCl_4 is physically unreasonable. The simultaneous fitting of molecular-kinetic model of each liquid shows that the model does not fit well with the high velocity regions of advancing and receding data (Figure 2.7b). Although the fitted equilibrium contact angles are reasonably closer to the measured value for each liquid, the molecular-kinetic model does not explain the asymmetry of the contact angles. From Figures 2.7a and 2.7b, it is observed that the molecular-kinetic model is suitable for low velocities while the hydrodynamic model is suitable for high velocities.²² Figure 2.7c shows the combined molecular-hydrodynamic model fitting, and the parameters are shown in Table 2.5. The combined model fits well with the entire velocity region and clearly explains the asymmetry of the advancing and receding data for all the liquids, but L_s value for CCl_4 is significantly smaller compared to molecular dimensions and also the K_w values for all the liquids are smaller in the order of magnitude. Petrov et al. recently studied the dynamic wetting behavior of a series of liquids (methanol, ethanol, 1-butanol,

and 1-octanol) on fluorinated mica surfaces, observed that the hydrodynamic model is suitable for capillary numbers ($Ca = \eta V/\gamma$) larger than 2×10^{-3} , and that the molecular-kinetic model is suitable for capillary numbers smaller than 5×10^{-4} .²⁴ Although the combined molecular-hydrodynamic model fits with the data in the entire capillary number region, it gives unreasonably small values for K_w . The three theoretical models, hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic, are not adequate to explain the partial wetting behavior of liquids, and “their conclusion is not universal”.²³

Figure 2.1. Liquid droplet on a solid surface (a) complete wetting ($\theta=0^\circ$) (b) partial wetting ($0^\circ < \theta < 90^\circ$) and (c) dewetting ($\theta > 90^\circ$)

Figure 2.2. Schematic representations of dynamic wetting models (a) Hydrodynamic²⁸
(b) Molecular-Kinetic³

Figure 2.3. Hydrodynamic model fitting for water advancing data [ref. 9, 26, and 21]

Figure 2.4. Molecular-kinetic model fitting for water advancing data on PET, for high-velocity curve, $\lambda = 0.36 \text{ nm}$, $K_w = 8.6 \times 10^9 \text{ sec}^{-1}$. For Low velocity curve, $\lambda = 1.1 \text{ nm}$, $K_w = 2.5 \times 10^5 \text{ sec}^{-1}$ [ref. 26]

Figure 2.5. Molecular kinetic model fitting for water advancing data [ref. 9, 26, and 21]

Table 2.1. Molecular-kinetic model parameters for water advancing data of Figure 2.5

Source of data	λ nm	$K_w \text{ sec}^{-1}$
Hayes and Ralston ⁹	0.99	9.2×10^6
Blake ²⁶	1.0	2.7×10^5
Petrov and Petrov ²¹	1.0	2.0×10^5

Figure 2.6. Comparison of all three models with advancing and receding contact angle data of OMCTS on fluoropolymer surfaces [ref. 13]

Table 2.2. Fitting parameters of all three models for OMCTS data, from Figure 2.6

Liquid movement	Hydrodynamic		Molecular-kinetic			Combined molecular-hydrodynamic			
	θ_o ($^\circ$)	L_s (nm)	θ_o ($^\circ$)	λ (nm)	K_w (sec $^{-1}$)	θ_o ($^\circ$)	λ (nm)	K_w (sec $^{-1}$)	L_s (nm)
Advancing	45.1 $\pm$ 0.3	1.8	42.5 $\pm$ 0.4	2.93 $\pm$ 0.1	(7.0 $\pm$ 1.3) $\times 10^5$	41.9 $\pm$ 0.6	5.2 $\pm$ 1.0	(6.1 $\pm$ 5.8) $\times 10^4$	73
Receding	33.9 $\pm$ 0.2	9.8	36.2 $\pm$ 0.3	1.7 $\pm$ 0.2	(4.0 $\pm$ 1.6) $\times 10^6$	37.3 $\pm$ 1.1	6.8 $\pm$ 1.0	(1.2 $\pm$ 1.4) $\times 10^4$	54

(a) Hydrodynamic model

(b) Molecular kinetic model

(c) Combined molecular-hydrodynamic model

Figure 2.7. Theoretical models fitting for advancing and receding data of CCl_4 ($\square$), tert-butanol (Δ) and OMCTS ($\diamond$) [ref. 22]

Table 2.3. Hydrodynamic model parameters for the data of Figure 2.7a

Liquid	L_s (advancing) [m]	L_s (receding) [m]
CCl_4	2.6×10^{-19}	5.7×10^{-14}
$(\text{CH}_3)_3\text{COH}$	5.6×10^{-10}	1.6×10^{-10}
OMCTS	4.2×10^{-9}	7.6×10^{-10}

Table 2.4. Molecular-kinetic model parameters for the data of Figure 2.7b

Liquid	Measure equilibrium contact angle ($^\circ$)	Equilibrium contact angle from fitting ($^\circ$)	λ [nm]	K_w [sec^{-1}]
CCl_4	58.1	58.9 ± 0.2	5.4 ± 0.2	$(1.0 \pm 2.6) \times 10^2$
$(\text{CH}_3)_3\text{COH}$	50.6	51.2 ± 0.4	5.0 ± 0.4	$(1.1 \pm 1.7) \times 10^3$
OMCTS	39.7	39.5 ± 0.3	5.0 ± 0.4	$(7 \pm 4) \times 10^3$

Table 2.5. Combined molecular-hydrodynamic model parameters for the data of Figure 2.7c

Liquid	Measure equilibrium contact angle ($^\circ$)	Equilibrium contact angle from fitting ($^\circ$)	λ [nm]	K_w [sec^{-1}]	L_s [m]
CCl_4	58.1	59.1 ± 0.2	8.1 ± 0.2	0.050 ± 0.002	2.7×10^{-14}
$(\text{CH}_3)_3\text{COH}$	50.6	50.8 ± 0.3	9.3 ± 0.4	0.076 ± 0.015	7.9×10^{-10}
OMCTS	39.7	40.0 ± 0.2	7.0 ± 0.5	707 ± 580	3.3×10^{-8}

EXPERIMENTAL METHODOLOGY

3.1 Materials

The solid surfaces used in contact angle measurements are cover glasses (Corning Inc., code no. 0211). These cover glasses (24 mm width, 40 mm height, and 0.186 mm thick) were purchased from Fisher Scientific. Cover glasses are smooth and uniform in terms of appearance. Cover glasses from the same batch (specified by the manufacturer) are used for all the measurements of a particular liquid. The glass plates are randomly selected from the box and were thoroughly blown with compressed air to remove any visible dust particles on the surface before every measurement. The consistency of cover glasses was evaluated by measuring the equilibrium contact angles of water on randomly selected glass plates; the contact angle was consistent within the standard deviation of $\pm 1^\circ$. Roughness of the glass plates is measured using an atomic force microscope (Molecular Imaging, in the tapping mode). The surface roughness of a randomly selected glass plate is ~ 1 nm. Figure 3.1 shows the AFM image of a bare glass plate.

For experiments investigating the viscosity effect, the bare cover glasses were coated with fluoropolymer using the following procedure. Fluoropolymer solution, 0.5% w/v was prepared by dissolving Teflon[®] AF1600 (from Dupont) in Fluorinated solvent FC75 (from 3M) solvent. This solution was used to coat the glass plates, which had been washed thoroughly with water and exposed to flame, and were immersed and taken out of the solution with a speed of 5 mm/min to a depth of 11 mm using a Kruss K100

tensiometer. The plate was dried in the open air for 3–4 hours to evaporate the solvent prior to the contact angle measurement. Although the morphology of the surface is different from the bare glass plate, the fluoropolymer coating does not seem to affect the roughness of the surface significantly. Roughness of the fluoropolymer coated cover glass is ~ 1 nm, shown in Figure 3.2.

Water (HPLC grade, cat. no W5-1), ethylene glycol (certified grade, cat. no E178-1), formamide (ACS certified, cat. no F84-1), and glycerin (100%, cat. no LC14850-2) were purchased from Fisher Scientific. In order to have a liquid with intermediate surface tension, 70% (by volume) of ethylene glycol was added to 30% of water and stirred using a motorized stirrer for 10 minutes. The surface tension of each liquid was measured using a Kruss K100 tensiometer in the Wilhelmy plate mode. Silicone oils of different viscosities, ranging from 5 cSt to 60,000 cSt, were obtained from Silicones Plus. The viscosity, density, and surface tension of all liquids are presented in Table 3.1. All of the liquids were used as received, without any further purification.

3.2 Measurement of Equilibrium Contact Angles

The equilibrium contact angles of each liquid on the glass plate were measured using a sessile drop method. A Rame-hart (model no 100-00) goniometer was used to measure the equilibrium contact angles. A schematic of the equilibrium contact angle measurement is shown in Figure 3.3. The specimen base was adjusted horizontally. Illumination from the lamp was adjusted to have better view of the droplet. Randomly selected cover glass from a box was blown with compressed air and placed on the

specimen stage. A small droplet (~ 0.1 ml) of liquid is placed on the specimen base from the micro-syringe.

As soon as a droplet came to equilibrium (stopped spreading on the surface), the protractor inside the microscope assembly was adjusted to one side of the droplet, and the angle between the solid surface and the tangent line of the liquid droplet is measured. The angle on the other side of the droplet was also measured by adjusting the protractor. This procedure is repeated by placing 4 to 5 droplets of the same liquid on the same substrate but at different areas and the angles between the tangent to each droplet and the solid surface were measured. The average of all the angles is taken as the equilibrium contact angle between the solid surface and the liquid. Contact angles between bare glass plates and different liquids (water, glycerin, formamide, pure ethylene glycol, and the mixture of ethylene glycol (70%) and water (30%)) and between fluoropolymer coated glass plates and silicone oils of different viscosities were measured in the same manner.

3.3 Measurement of Dynamic Contact Angles

Dynamic contact angle measurements were performed using a Kruss K100 tensiometer. The schematic illustration of a tensiometer is given in Figure 3.4. The Kruss K100 tensiometer is an ideal instrument for measuring small changes in contact angles with a wide range (0.1 - 450 mm/min) of velocity changes. It consists of a sensitive balance (sensitivity ~ 0.001 mg), which measures the force exerted by a liquid on the solid surface. The liquid vessel can be moved in both directions, up (advancing) and down (receding), with a specified speed using a built-in motorized platform. Both the

balance and the motorized platform are connected to a personnel computer (PC) for data acquisition and automatic control, operated with Lab Desk 2.0 software. Although the tensiometric method is an indirect method of contact angle measurement, it is one of the most accurate methods to measure small changes in contact angles, as explained in Chapter II. Force versus distance data at constant speed is obtained; and the contact angle is calculated from the force by using the following formula:⁶

$$\cos\theta = \frac{F - F_b}{L\gamma_{lv}} \quad (3.1)$$

where, F is the force exerted by the liquid on the solid surface, F_b is the buoyancy force, L is the wetted length (circumference) of solid surface, γ_{lv} is the liquid surface tension, and θ is the contact angle.

The liquid is filled up in the vessel and placed on the motorized platform. Both sides of the cover glass are cleaned with compressed air and it is fixed to the sample holder. The measurement configurations (dimensions of the cover glass, liquid properties, procedure of the measurement) are specified to the software. The cover glass is adjusted vertically and the liquid vessel is raised close (approximately 2 mm) to the bottom of the cover glass. The position and force on the cover glass are zeroed by unlocking the balance clamp. Immediately after clicking the start command on the measurement window of the PC, the liquid vessel will move upward (advancing) with a given speed until the cover glass reaches its specified depth (10 mm for all the measurements here). After waiting for a second, the vessel moves downward (receding) with the same speed. A typical force versus distance curve for advancing and receding movement is obtained

as shown in Figure 3.5. The three phase contact line shape for different contact angles is schematically shown in Figure 3.6.

The force was linearly decreased in the advancing movement and increased in the receding movement with distance. The buoyancy force can be neglected by extrapolating the linear force slope to zero distance. The exact force exerted by the liquid ($F-F_b$) onto the solid surface was directly obtained, and this force was used to calculate the dynamic contact angle by Equation 3.1. This procedure was repeated for each measurement. Every time a new plate was used and liquid in the vessel was replaced to avoid contamination. Each measurement was repeated two to four times to check the consistency of the measurement.

Figure 3.1. Atomic force microscope picture of a plain cover glass

Figure 3.2. Atomic force microscope picture of a fluoropolymer coated glass plate

Table 3.1. Physical properties of different liquids used in dynamic contact angle analysis

Liquid	Viscosity (cP) ¹	Density (g/cm ³) ¹	Surface Tension(mN/m) ²
Water (HPLC)	0.995	0.998	72.8
Glycerin	924.27	1.263	65.2
Formamide	3.2	1.113	58.2
Ethylene glycol +30% water	8.66	1.06	53.4
Ethylene glycol	21.81	1.109	48.20
Silicone Oil ³	5	0.91	19.7
	10	0.93	20.1
	20	0.95	20.6
	50	0.96	20.7
	100	0.973	20.9
	350	0.973	21.1
	1,000	0.973	21.1
	5,000	0.973	21.1
	10,000	0.973	21.1
	60,000	0.973	21.1

¹ Viscosity and density of each liquid are specified by the supplier

² Surface tension of each liquid was measured using Wilhelmy plate method

³ All the properties (including surface tension) of silicone oils are supplier's specifications and the viscosity is in centi stokes.

Figure 3.3. Equilibrium contact angle measurement using a Goniometer

* Part of the Figure is From Website: <http://www.ipfdd.de/research/res12/Sessile.jpg>

Figure 3.4. Schematic illustration of KRUSS K100 Tensiometer

Figure 3.5. Force versus distance trace in a wetting cycle

Figure 3.6. Shape of the three phase contact region for different contact angles

Chapter IV

EXPERIMENTAL RESULTS AND DISCUSSION

Equilibrium contact angles of all the liquids are measured on bare glass plates or fluoropolymer coated glass plates using a goniometer as explained in Chapter III, and the values are presented in Table 4.1. The equilibrium contact angle is different for each simple liquid, depending on the liquid properties such as surface tension and the interactions between liquid and solid substrates. The viscosity of the silicone (PDMS) oil seems to have only a minor influence on the equilibrium contact angles, since the surface tension of oils does not change significantly with the viscosity.

The dynamic contact angles are measured in advancing and receding movement for all liquids using a Kruss K100 Tensiometer as described in Chapter III. The following sections discuss the fitting of theoretical models with experimental data as well as the contact angle hysteresis.

4.1 Comparison with Hydrodynamic Model

The hydrodynamic model, Equation 2.3 in Chapter II, gives rise to a linear fit, when the cube of dynamic contact angle is plotted as a function of contact velocity. The characteristic capillary length (L) value in Equation 2.3 is calculated from the Laplace equation $[L = (2\gamma_{lv}/\rho g)^{1/2}]$.¹³ The hydrodynamic model does not necessarily require the equilibrium contact angle as an input, instead, the fitting generates equilibrium contact angles and the model parameter, slip length, L_s .⁹ The equilibrium contact angle can be

obtained from the cubic root of the intercept and the slip length (L_s) value can be obtained from the slope of the linear fit.

4.1.1 Fitting with Experimental Data of Simple Liquids

The hydrodynamic model does not fit well with the dynamic contact angles of simple liquids. For example, experimentally, advancing contact angle of water increases with speed and reaches a plateau, as shown in Figure 4.1 (inset of Figure 4.1 shows the cube of the advancing contact angles versus the speed). The hydrodynamic model does not explain the plateau region, and only fit reasonably well for the low velocity region (0.5 – 25 mm/min). The equilibrium contact angle from the fitting, 54.25° , is reasonably close to the measured value, 54.1° ; however, the slip length (L_s) value from the slope (in the order of sub-atomic dimensions) is not comparable to the molecular dimensions and not physically reasonable.

Similarly, for other simple liquids (glycerin, formamide, ethylene glycol, and mixture of ethylene glycol (70%) and water (30%)), the advancing contact angle increases with speed before reaching a plateau. The contact velocity required to reach contact angle plateau and the plateau value are different for each liquid. The hydrodynamic model does not fit over the entire velocity range, as shown in Figure 4.2. Although the equilibrium contact angles for each liquid from the hydrodynamic model fitting at the low velocity region are close to the measured values, the slip length (L_s) values from the slopes, again, are not physically reasonable, in the order of subatomic dimensions. The receding contact angle data for all simple liquids (not presented here) is

more scattered than the advancing contact angles, and does not fit well with hydrodynamic model. The model gives physically unreasonable values for the slip length (L_s), and the equilibrium contact angle values from the fitting are 15° – 20° smaller than the measured values. This observation is in agreement with Hayes and Ralston's study of a glycerin and water mixture on PET surfaces (the contact angle plateau did not appear in their results); they observed similar equilibrium contact angles from the model and experiment in the advancing case, but the measured equilibrium contact angle in the receding case is significantly different from the fitting. The slip length (L_s) values are "significantly smaller than the molecular dimensions" for both the advancing and receding cases.⁹ Similarly, the slip length (L_s) values for simple liquids, obtained by Shneemilch et al. (hexadecane on fluoropolymer surface) and Petrov et al. (CCl_4 , on fluorinated mica surface, Table 2.3 in Chapter II), are smaller than the molecular dimensions.^{13,22}

As discussed above, the relationship between cube of the dynamic contact angle and the velocity, for the simple liquids is not a single linear function with unique slope in the entire region. In the hydrodynamic model fitting, the viscous friction term ($9\eta V/\gamma_{lv}$) is much lower, in the order of 10^{-6} – 10^{-3} , except for glycerin (10^{-3} – 10^{-1}), than the equilibrium contact angle term (θ_o^3). Therefore, the contribution of this term in the model is very small, even for much higher $\ln(L/L_s)$ values, for the simple liquids observed here. This could be the reason that the hydrodynamic model does not explain the relationship between dynamic contact angles and contact velocity for simple liquids. Although the viscous friction term ($9\eta V/\gamma_{lv}$) is in the order of 10^{-3} – 10^{-1} , the hydrodynamic model does

not explain the contact angle plateau for glycerin. Overall, the hydrodynamic model does not adequately describe the experimental contact angle data for simple liquids observed here.

4.1.2 Fitting with Experimental Data of Polydimethylsiloxane (PDMS) Oils

Figure 4.3a shows the raw data of the advancing contact angles of PDMS oils on fluoropolymer coated glass plates. The advancing contact angle for higher viscosity oils reaches its maximum value of 180° , while the contact line speed to attain 180° is decreased as viscosity is increased. Figure 4.3b shows the linear relationship between the cube of the advancing contact angle and contact velocity for oils with different viscosities. The hydrodynamic model fits reasonably well in terms of linear relationships and the fitting parameter, slip length (L_s), values for different viscosity oils are included in Table 4.2. Although the slip length (L_s) value for 5 cSt oil is physically unreasonable, the value increases with the increasing viscosity of the oil. The L_s values for 100 cSt, 1,000 cSt, 10,000 cSt, and 60,000 cSt oils are larger than the molecular dimensions, and the equilibrium contact angles from the hydrodynamic fitting are significantly different from the measured values.

Table 4.2 also includes the stretched chain lengths and radii of gyration values of PDMS oils. As discussed in Chapter II, the slip length (L_s) value should be 1-2 layers of molecules on the solid surface.³⁰ The slip length value for 5 cSt oil is physically insignificant and much smaller than the linear chain length and radius of gyration. For oils with a viscosity of 100 cSt, 1,000 cSt, 10,000 cSt and, 60,000 cSt, even the slip

length values are similar to the order of stretched linear chain lengths, it is hard to imagine that the molecules are pinned to the surface at one end, fully stretched at the other end, and moving along the surface. It seems more reasonable to hypothesize that the molecules form multi-layers in the immediate vicinity of the solid surface instead of moving in stretched form. In the present study the data suggests that for oils with viscosities ranging from 5 cSt to 60,000 cSt, the slip meniscus comprises 8 - 200 layers if the inconsistency between measured and fitted equilibrium contact angles is neglected. This observation suggests that the magnitude of L_s is not in agreement with the theory, for the investigated oils with different viscosities on fluoropolymer surfaces.

Figure 4.4a shows the receding contact angles for oils of different viscosities as a function of contact velocity. The receding contact angles of oils initially decrease with velocity and then reach their minimum value of 0° . The velocity required to reach 0° decreases significantly with increasing viscosity. Figure 4.4b shows the hydrodynamic model fitting for receding contact angles of different viscosity oils. The model fits reasonably well in terms of the linear relationship, and the fitted parameter values for receding contact angles of different viscosity oils are shown in Table 4.3. Interestingly, for 100 cSt oil the equilibrium contact angle from the fitting is the same as the measured value and the slip length value is similar to the radius of gyration value; this coincidence might be purely incidental. For oils with viscosities of 1,000 cSt, 10,000 cSt, and 60,000 cSt, the fitted equilibrium contact angles are much lower than the measured values, and the slip length (L_s) values are higher than the order of molecular dimensions.

The equilibrium contact angles from the hydrodynamic model fitting differ from the advancing case to the receding case for all the oils of different viscosities. The slip length (L_s) values for 100 cSt, 1000 cSt, 10000 cSt, and 60000 cSt are 1-2 orders of magnitude less in the advancing case than receding case. The difference in slip length values for advancing and receding cases is also evidenced by Shneemilch et al.¹³ (hexadecane and OMCTS on fluoropolymer surfaces) and Petrov et al.^{22,23} (CCl_4 , butyl alcohol, methanol etc., on fluorinated mica surfaces). The reason for the difference is that the change in the advancing contact angle with velocity is not symmetric to the change in receding contact angle, with respect to zero contact line speed for all the oils.

The viscosity effect on dynamic contact angles is further investigated by conducting experiments with changing the viscosity of the oil while maintaining constant speeds of 10 mm/min and 300 mm/min, as shown in Figure 4.5. The advancing contact angle increases with viscosity at constant speed and reaches its maximum value (180°), and the receding contact angle decreases with viscosity and reaches 0° when the viscosity of the oil increases to a certain value. For 10 mm/min, the advancing contact angle reaches its maximum (180°) at the oil viscosity 45,000 cSt, and the receding contact angles reaches its minimum (0°) at 350 cSt. For 300 mm/min, the advancing contact angle reaches 180° at 2,500 cSt, and receding contact angle reaches 0° at 50 cSt well before the advancing contact angle reaches 180° . Although advancing and receding contact angle values at constant speeds seem to meet at low viscosity values, the dynamic contact angles do not change symmetrically in the advancing and receding movement.

Finally, the advancing and receding contact angles of PDMS oils over fluoropolymer coated plates are plotted as functions of the capillary number ($Ca = \eta V / \gamma$) as shown in Figure 4.6a. The advancing contact angle increases with increasing capillary number and reaches its maximum value (180°) at high capillary numbers whereas the receding contact angle decreases with increasing capillary numbers and reaches its minimum value (0°). The advancing and receding contact angles are not mirror images of each other in terms of capillary numbers. Further more, the L_s values are calculated using the measured equilibrium contact angles and the hydrodynamic model (Equation 2.3), point by point (not the overall curve fitting). Based on the calculated L_s values, a master curve of L_s versus capillary numbers is generated and shown in Figure 4.6b. For low and high capillary numbers, the L_s values are not physically reasonable, either much smaller or much larger (even in the range of mm) than the molecular dimensions. From this observation one can conclude that the hydrodynamic model is not applicable for the entire velocity and viscosity regions of the observed systems. There may be a range of capillary numbers, where the hydrodynamic model gives physically reasonable slip length values. Petrov et al. observed (methanol, ethanol, butanol, and octanol on fluoropolymer surfaces) that the hydrodynamic model is applicable only for the capillary numbers above 2×10^{-3} .²³ This work also observed the minimum limit is in the order of 10^{-3} and suggested a maximum limit for the capillary numbers qualitatively (depending on the magnitude of the inner region, this limit may change). This conclusion may not be universal; further experimental investigations are needed to confirm the limit.

4.2 Comparison with Molecular-Kinetic Model

The molecular-kinetic model (Equation 2.4 in Chapter II) describes the dynamic wetting behavior of a liquid as the adsorption and desorption process of molecules near the three phase contact line. The model uses the measured equilibrium contact angle as an input and gives two model parameters (λ , K_w) as outputs. By the adherence of the dynamic contact angle data to the molecular-kinetic model, the values of λ and K_w should be physically reasonable. As explained in Chapter II, the parameters, λ and K_w represent the length and quasi equilibrium rate constant for molecular displacement, respectively. The measured equilibrium contact angles listed in Table 4.1 will be used in the fitting of the molecular-kinetic model for both advancing and receding cases.

4.2.1 Fitting with Experimental Data of Simple Liquids

The advancing contact angle data for all liquids are fitted using the POLYMATH 5 software program in the least square nonlinear regression mode. A single curve fit is used for the entire velocity region. Figure 4.7 shows the advancing contact angle data of all simple liquids investigated here (water, glycerin, formamide, ethylene glycol, and mixture of ethylene glycol and water) as functions of contact velocity along with the molecular-kinetic model fitting. The model fits reasonably well with the data for all liquids, except in the intermediate velocity region of water. The parameters (λ and K_w) for each liquid from the non-linear regression analysis are listed along with some physical properties of the liquids in Table 4.4. Although a broader velocity range is applied in this study than the velocity range observed by Petrov and Petrov²¹ (water and

aqueous glycerol on PET), a single set of parameters are obtained for the entire velocity range in this study which contradicts with the two sets of parameters obtained by Petrov and Petrov.²¹ The λ values are physically reasonable: in the order of a nanometer for all the simple liquids. The parameter λ is often considered as the distance between adsorption sites on the solid surface, but it is possible that on a fairly homogenous solid surface, this value slightly depends on the liquid properties such as molecular volume.¹³

In Table 4.4, the K_w values do not seem to have a direct correlation with the liquid surface tension, but it may incorporate other additional parameters such as liquid viscosity. The K_w values, for the liquids observed here, are in the order of 10^4 - 10^2 sec^{-1} , and for the similar systems observed by J.G. Petrov²¹ (water on PET surface), R.A.Hayes⁹ (water and mixture of glycerin and water on PET surfaces), and M. Shneemilch et al.^{13,22} (hexadecane and octamethylcyclotetrasiloxane on fluorinated surface), the K_w values are in the order of 10^6 - 10^3 sec^{-1} and are considered to be reasonable. Although “for the simple liquids, the rate constant for bulk viscous flow is in the order of 10^{11} sec^{-1} ”,²⁶ the K_w values are many orders of magnitude lower. Since the K_w represents the quasi equilibrium rate constant for wetting without applying force (“natural frequency of wetting”), it is obvious that K_w is much smaller than the bulk liquid rate constant.³¹ The reciprocal values of K_w represent the relaxation times of molecules on the solid surface.²⁶ The relaxation times for the liquids observed here are many orders of magnitude higher when compared to the relaxation times of liquid molecules in the bulk phase. This suggests that the interactions between liquid molecules and solid surface are much stronger than the interactions between molecules in bulk

liquid phase. The recent study of Petrov et al.²² claimed that it is reasonable to consider parameters λ and K_w in a combined form, instead of considering them separately. They combined parameters in the form of A ($kT/\gamma\lambda^2$), the ratio between thermal energy and surface free energy per unit molecule, and B ($2K_w\lambda/(\mu v/h)$), characteristic velocity. In the present study, the constant A is calculated in Table 4.4, this value is much smaller than unity which indicates that the surface energy is larger than the thermal energy for all the liquids observed here.

The receding data of simple liquids is more scattered than the advancing case. POLYMATH 5 does not give a good fit for all the data points in terms of a single curve. Thus the molecular kinetic model fitting is performed using the best fitting of the model to each point by MICROSOFT EXCEL. Figure 4.8 shows the molecular kinetic model fitting of receding data for simple liquids. In contrast with all other liquids, water's receding contact angle is increasing with speed, whereas the receding contact angles of other liquids are decreasing with speed and reaching the minimum value, 0° . The reason for this receding behavior of water is unknown, but the model fits reasonably well with data for the given parameters, if ignoring the trend. The model also fits reasonably well with the receding data of other simple liquids. The parameters obtained for all liquids are presented in Table 4.5. Similar to the advancing case, the λ values are in the order of nanometer, and K_w values are in the order of 10^6 - 10^3 sec^{-1} .

The parameters λ and K_w differ significantly in advancing and receding cases; the λ values are in the same order of magnitude with different numerical values, whereas K_w values are 1-2 orders magnitude higher in the receding case than in the advancing case.

The differences in the fitted parameters in the advancing and receding cases are also observed by Shneemilch et al.¹³ and Petrov et al.²² This difference has been attributed to the fact that the advancing and receding contact angles are not exact mirror images with respect to the zero contact line velocity. The simultaneous fit of advancing and receding branches shows that the molecular-kinetic model is not adequate enough to explain the asymmetry of the advancing and receding contact angles.^{22,23} This observation may question the molecular-kinetic model's assumption that "irrespective of whether the adsorption site is occupied by the advancing phase or receding phase, the same amount work is done on each site", which means that the parameters, λ and K_w , must be the same in both advancing and receding cases.^{4,23} The difference in λ values for advancing and receding cases, observed in the present work, supports the conclusion that λ may not only be the distance between adsorption sites.²²

4.2.2 Fitting with Experimental Data of PDMS Oils

Figure 4.9 shows the molecular kinetic model fitting for the advancing data of PDMS oils of different viscosities. The model does not fit with 5 cSt data; it overestimates the contact angle and velocity relationship. Although the model fits reasonably well with 100 cSt and 1,000 cSt data and low velocity regions of 10,000 cSt and 60,000 cSt oils, it does not estimate the exact velocity to reach 180° . For 60,000 cSt, the model predicts a high value (28 mm/min) for velocity to reach 180° , but the experimental data suggest that the contact angle reaches 180° at a lower contact velocity (12.5 mm/min). The molecular kinetic model parameters are shown in Table 4.6; the λ

values are physically reasonable, between 0.99 – 2 nm for all the oils. The K_w values are in the order of 10^2 - 10^5 sec^{-1} ; viscosity seems to have a significant influence on the K_w value, when the surface tension remains relatively constant. The K_w value decreases with increasing viscosity, except for 1,000 cSt. The constant A value is less than unity for all the PDMS oils in the advancing case, which means that the surface energy is dominant when compared to the thermal energy.

Figure 4.10 shows the molecular-kinetic model fitting for the receding data of PDMS oils. The receding contact angles of PDMS oils decrease with speed and reach 0° , the molecular kinetic model fits reasonably well with the data of 100 cSt and 1,000 cSt before the receding contact angle reaches 0° . Since, the receding contact angles of 10,000 cSt and 60,000 cSt reaches 0° at very low velocities (1 mm/min and 0.5 mm/min, respectively), the model fitting for these data is not presented. The receding molecular kinetic model parameter values for 100 cSt and 1,000 cSt are presented in Table 4.7. The λ and K_w values for 100 cSt and 1,000 cSt data are significantly different from their respective values in the advancing case, where they are in the same order of magnitude. The reason for the difference in the parameters values for advancing and receding data is clear, since the molecular kinetic model does not explain the asymmetry of the data. Overall, the molecular kinetic model does not fit well with the dynamic contact angle data of PDMS oils. Limited literature is available on the molecular kinetic model comparison to the viscosity data.³ The present work is the first, to the best of knowledge, on the direct comparison of the molecular kinetic model to the viscosity data, and the viscosity range of the oils used in this study (5 cSt – 60,000 cSt) is broader than the T. D.

Blake's observations (1.5 cSt – 104.3 cSt) of aqueous glycerol solutions on PET surfaces.³

4.3 Comparison with Combined Molecular-Hydrodynamic Model

The combined molecular-hydrodynamic model is the combination of the molecular kinetic and hydrodynamic Equations as explained in Chapter II. The combined equation can be written as⁵

$$(\theta_d)^3 = \left\{ \arccos \left[\cos \theta_o \mp \left(2nkT / \gamma_{lv} \lambda^2 \right) \arcsin h(V / 2K_w \lambda) \right] \right\}^3 \pm (9\eta V / \gamma_{lv}) \ln(L / L_s). \quad (4.1)$$

All the constants and parameters are of their usual significance as explained in previous sections. The fitting of this model with the experimental data generates the three independent parameters, λ , K_w , and L_s .

4.3.1. Fitting with Experimental Data of Simple Liquids

The combined molecular-hydrodynamic model fits reasonably well with the advancing contact angle data of simple liquids in terms of curve fitting. Figure 4.11 shows the combined model fitting for simple liquids' advancing contact angle data and the parameters', λ , K_w , and L_s , values are presented in Table 4.8. The λ values are physically reasonable: in the order of a nano meter for all the liquids. Remarkably, λ and K_w values do not deviate significantly from the values fitted using the molecular kinetic model. The slip length (L_s) values are not physically reasonable for all of the simple liquids. Since the hydrodynamic term ($9\eta V / \gamma_{lv}$) in Equation 4.1 is in the order of 10^{-6} - 10^{-3} for all of the simple liquids, except glycerin, the L_s values can vary anywhere from the

sub-atomic order to the macroscopic order. This does not affect the final contact angle values from the model. Although the hydrodynamic term for glycerin is in the order of 10^{-3} - 10^{-1} , the L_s value is not practically meaningful. This indicates that λ and K_w are the main influential parameters in the combined model for all simple liquids observed here.

Overall, the combined model is not superior compared to the molecular-kinetic model for the investigated simple liquids. This observation questions the nonhydrodynamic velocity dependence of the equilibrium contact angle for simple liquids observed here, as described by the combined model. This is in accordance with the conclusion, “the velocity dependence of the equilibrium contact angle is specific for any system”⁵ and contradicts with the conclusion that the combined molecular-hydrodynamic model best describes dynamic wetting behavior.^{13,22}

Figure 4.12 shows the combined model fitting for the receding data of simple liquids. The model fits reasonably well for the given parameters in terms of the curve fitting; the parameters are given in Table 4.9. The λ and K_w values are the same as in the molecular kinetic model. Also, the λ values for different simple liquids are in the same order magnitude, whereas the K_w values change with liquid properties. Interestingly, L_s values are not similar to those from the hydrodynamic model fitting. The L_s value for water (not a specific value) can be anywhere from the sub-atomic order to the macroscopic order of magnitude. Since the hydrodynamic term in Equation 4.1 ($9\eta V/\gamma_{lv}$) is very small, in the order of 10^{-6} - 10^{-3} , and the contact angle increases with speed in contrast to the other liquids. For other simple liquids it is interesting to observe that the L_s value is equal to their characteristic capillary length (L).

The parameters of the combined model, λ , K_w , and L_s , are different in the advancing and receding cases for all of the simple liquids observed here. The difference in parameters for advancing and receding cases is also evident in the study of Shneemilch et al.¹³ The reason is unknown, though it could be due to the fact that the separate curve fits using a single measured equilibrium contact angle value for both advancing and receding cases. Petrov et al.²³ observed a series of liquids (methanol, ethanol, 1-butanol, and 1-octanol) on fluoropolymer surfaces and simultaneously fitted the advancing and receding contact angles to get a single parameter set for both the advancing and receding cases. The combined model explains the asymmetry of contact angles in advancing and receding cases, but the parameters obtained by them are not physically reasonable. Although their conclusion is specific for their system, they concluded that all three models in their present form are not sufficient to explain the partial wetting behavior of liquids.²³

4.3.2 Fitting with Experimental Data of PDMS Oils

Figure 4.13 shows the fitting of the combined molecular-hydrodynamic model for PDMS advancing contact angle data; the parameters are given in Table 4.10. The combined model fits reasonably well with the entire range of advancing contact angle data for all PDMS oils in terms of curve fitting. It also explains the 180° contact angle region for 10,000 cSt and 60,000 cSt, unlike the molecular kinetic model, but this model also predicts the velocity to reach the maximum contact angle (180°) for 1,000 cSt oil as higher than the experimental value. The λ values are in the same order of magnitude for

all the liquids, but they are significantly different from the molecular-kinetic model results. The K_w values differ significantly from liquid to liquid and the trend is hard to interpret from practical perspective. The hydrodynamic parameter (L_s) value also does not follow any trend. The value is in the order of molecular dimensions for 100 cSt, 1,000 cSt, and 10,000 cSt oils, but it is in the order of micro-meter for 60,000 cSt oil. This work provides the first comparison of the combined model with a wide range (5 cSt – 60,000 cSt) of viscosity data.

Figure 4.14 shows the combined model fitting for the receding data of PDMS oils; the model fits reasonably well with 100 cSt and 1,000 cSt data in terms of the curve fitting. The model predicts the velocity to reach the 0° contact angle as lower than the experimental value and it does not explain the plateau of the 0° contact angle. Since, the receding contact angle for 10,000 cSt and 60,000 cSt oils reach 0° at 1 mm/min and 0.5 mm/min, there is not enough data for model fitting. The parameters for the receding data of 100 cSt and 1,000 cSt oils are presented in Table 4.11; the λ value for both of the oils is similar and higher than the value in the advancing case. The K_w values are also significantly different from advancing case, and the value is higher for 100 cSt than for 1,000 cSt. The L_s value is in the order of molecular dimensions for both 100 cSt and 1,000 cSt oils in the receding case.

4.4 Contact Angle Hysteresis

Contact angle hysteresis, the difference between advancing and receding contact angles, is the measure of the roughness and heterogeneity of a solid surface.^{3,11} The

surface heterogeneity and roughness affect the displacement of molecules at the three phase boundary, thus the contact line may not be in equilibrium (“metastable”) during the advancing and receding movements.¹¹ These small variations in displacement due to the heterogeneity will result in different contact angles, when compared to a perfectly smooth and homogenous surface. Figure 4.15 shows the hysteresis changing with speed for simple liquids investigated in this work. The hysteresis increases with speed for all the simple liquids before reaching a plateau. Contact angle hysteresis is significant for all the liquids even at very low velocities. The thermodynamic model does not take the kinetic dependence of hysteresis into account,³² but this study strongly suggests that the contact angle hysteresis also changes with contact line speed. Although the contact angles are measured on the same kind of substrates, the plateau values of contact angle hysteresis are different for each liquid observed here. This proves that hysteresis is also caused by the interactions between the contact liquid and the solid substrates.³³

Figure 4.16(a) shows the change in hysteresis with speed for different viscosity oils. For 5 cSt oil, the hysteresis does not change significantly with speed; for 100 cSt and 1,000 cSt oils, hysteresis increases with speed. For 10,000 cSt and 60,000 cSt oils, the receding contact angle reaches 0° at 1 mm/min and 0.5 mm/min, respectively, thus the hysteresis is the same as the advancing contact angle. Figure 4.16(b) shows the change in hysteresis with viscosity at constant speeds of 10 mm/min and 300 mm/min. Hysteresis increases with speed and reaches 180° at high viscosities; the viscosity to reach 180° is smaller for the higher speed, 300 mm/min, than the lower speed, 10 mm/min. The contact angles of PDMS oils are measured on fluoropolymer coated glass plates; the coating does

not significantly effect the roughness of the surface as shown in Figures 3.1 and 3.2 (Chapter III). The surface looks uniform in terms of appearance. This work suggests that hysteresis strongly depends on solid-liquid interactions and reports the dependence of hysteresis on liquid viscosity for the first time.

Table 4.1. Equilibrium contact angle of each liquid on substrates

Liquid	Surface tension (mN/m)	Equilibrium contact angle (°)	
Water (HPLC) ¹	72.8	54.1 ± 1.1	
Glycerin ¹	65.2	46.0 ± 1.5	
Formamide ¹	58.2	30.5 ± 2.0	
Ethylene glycol +30% water ¹	53.4	36.6 ± 0.5	
Ethylene glycol ¹	48.20	33.5 ± 0.5	
Silicone(PDMS) Oil ²	Viscosity (cSt)	Surface tension (mN/m)	Contact angle(°)
	5	19.7	46
	10	20.1	47
	20	20.6	49
	50	20.7	50
	100	20.9	49
	350	21.1	51
	1,000	21.1	51
	2,500	21.1	52
	5,000	21.1	52
	7,500	21.1	52
	10,000	21.1	52
	25,000	21.1	52
	45,000	21.1	52
	60,000	21.1	52

¹ Equilibrium contact angles were measured on bare coming glass plates

² Equilibrium contact angles of silicone (PDMS) oils were measured on fluoropolymer coated glass plates

Figure 4.1. Water advancing contact angle as a function of contact velocity, inset is the hydrodynamic model fitting for experimental data

Figure 4.2. Hydrodynamic model fitting for advancing contact angles of simple liquids

Figure 4.3. Advancing contact angles of different viscosity oils (a) raw data as a function of contact speed (b) Hydrodynamic model fitting

Table 4.2. Hydrodynamic model parameters for advancing data of different viscosity oils

Viscosity (cSt)	Equilibrium contact angle (measured)	Equilibrium contact angle (from fitting)	Capillary length, L (m)	Slip length, L _s (m)	Fully stretched chain length (m)	Radius of gyration (m)*
5	46.5	50.81	2.0905×10^{-3}	6.778×10^{-48}	3.4808×10^{-9}	4.017×10^{-10}
100	49	58.54	2.1079×10^{-3}	1.7412×10^{-8}	1.938×10^{-8}	1.206×10^{-9}
1,000	51	61.81	2.1069×10^{-3}	5.3658×10^{-8}	1.052×10^{-7}	2.544×10^{-9}
10,000	52	71.25	2.1037×10^{-3}	5.0295×10^{-7}	2.274×10^{-7}	3.816×10^{-9}
60,000	52	65.2	2.1037×10^{-3}	1.6329×10^{-6}	3.549×10^{-7}	4.688×10^{-9}

* Radius of gyration is calculated from $\langle R_g \rangle = (nl^2/6)^{1/2}$, where n is the number of chain segments and l is the bond length³⁴

Figure 4.4. Receding contact angles of oils of different viscosities (a) raw data
(b) Hydrodynamic model fitting

Table 4.3. Hydrodynamic model parameters for receding data of oils with different viscosities

Viscosity (cSt)	Equilibrium contact angle (measured)	Equilibrium contact angle (from fitting)	Capillary length, L (m)	Slip length, L _s (m)	Fully stretched chain length (m)	Radius of gyration (m)
100	49	48.16	2.1079×10^{-3}	1.13×10^{-9}	1.938×10^{-8}	1.206×10^{-9}
1,000	51	46.95	2.1069×10^{-3}	3.517×10^{-6}	1.052×10^{-7}	2.544×10^{-9}
10,000	52	44.22	2.1037×10^{-3}	2.729×10^{-6}	2.274×10^{-7}	3.816×10^{-9}
60,000	52	35.27	2.1037×10^{-3}	6.83×10^{-4}	3.549×10^{-7}	4.688×10^{-9}

Figure 4.5. Dynamic contact angles change with viscosity at constant speeds

Figure 4.6. Master curves for (a) Contact angles as function of capillary number for all viscous oils (b) L_s values calculated using hydrodynamic equation

Figure 4.7. Molecular-kinetic model fitting for advancing contact angles of simple liquids

Table 4.4. Molecular kinetic model parameters for simple liquids, in the advancing case

Liquid	Surface Tension (mN/m)	Viscosity (Cp)	Equilibrium Contact angle(°)	λ (nm)	K_w (sec ⁻¹)	A ($2kT/\gamma\lambda^2$)
Water	72.8	0.995	54.1 ±1.1	1.0225	1.19×10^4	0.1081
Glycerin	65.2	924.27	46.0 ±1.5	0.884	3.13×10^3	0.1615
Formamide	58.2	3.81	30.5 ±2.0	1.0665	5.53×10^4	0.1243
Ethylene glycol + 30% water	53.4	8.66	36.6 ±0.5	1.46	3.109×10^2	0.07229
Ethylene glycol	47.7	21.81	33.5 ±0.5	1.47	1.9664×10^3	0.07983

Figure 4.8. Molecular kinetic model fitting for receding contact angles of simple liquids

Table 4.5. Molecular kinetic model parameters for receding data of simple liquids

Liquid	Surface tension (mN/m)	Viscosity (Cp)	Equilibrium Contact angle(°)	λ (nm)	K_w (sec ⁻¹)	A ($2kT/\gamma\lambda^2$)
Water	72.8	0.995	54.1±1.1	0.386 ±0.205	(1.069 ±0.027)×10 ⁶	1.918 ±2.946
Glycerin	65.2	924.27	46.0 ±1.5	1.147 ±0.284	(6.55±1.06)×10 ³	0.1135 ±0.0572
Formamide	58.2	3.81	30.5±2.0	0.614 ±0.21	(12.235±12.2) ×10 ⁵	0.295 ±0.077
Ethylene glycol + 30% water	53.4	8.66	36.6±0.5	1.78 ±0.439	(12.073±7.35)×10 ³	0.0601 ±0.039
Ethylene glycol	47.7	21.81	33.5 ± 0.5	2.114 ±0.597	(7.6575±0.928)×10 ³	0.106 ±0.017

Figure 4.9. Molecular kinetic model fitting for PDMS oils advancing contact angle data

Table 4.6. Molecular kinetic model parameters for advancing data of PDMS oils

PDMS oil viscosity (cSt)	Surface tension (mN/m)	Equilibrium contact angle (°)	λ (nm)	K_w (sec ⁻¹)	A ($2kT/\gamma\lambda^2$)
5	19.7	46.5	1.94312	1.368×10^5	0.11063
100	20.9	49	1.99038	1.9052×10^4	0.09938
1,000	21.1	51	1.08247	6.474×10^4	0.3328
10,000	21.1	52	0.98637	1.1032×10^4	0.40083
60,000	21.1	52	1.20448	9.754×10^2	0.2688

Figure 4.10. Molecular kinetic model fitting for receding data of PDMS oils

Table 4.7. Molecular kinetic model parameters for receding data of PDMS oils

PDMS oil viscosity (cSt)	Surface tension (mN/m)	Equilibrium contact angle (°)	λ (nm)	K_w (sec ⁻¹)	A
100	20.9	49	0.25	4.469×10^7	6.2995
1,000	21.1	51	1.3	2.510×10^4	0.231

Figure 4.11 Combined molecular-hydrodynamic model fitting for advancing contact angles of simple liquids

Table 4.8. Combined molecular-hydrodynamic model parameters for advancing contact angle data of simple liquids

Liquid	Surface Tension (mN/m)	Viscosity (Cp)	Equilibrium Contact angle	λ (nm)	K_w (sec ⁻¹)	L_s (m)	L (mm)
Water	72.8	0.995	54.1 $\pm$ 1.1	1.025	0.0119 $\times$ 10 ⁶	*	3.85
Glycerin	65.2	924.27	46.0 $\pm$ 1.5	0.8073	5.298 $\times$ 10 ³	1.362	3.25
Formamide	58.2	3.81	30.5 $\pm$ 2.0	1.0515	5.568 $\times$ 10 ⁴	*	3.24
Ethylene glycol + 30% water	53.4	8.66	36.5 $\pm$ 0.5	1.2545	1.248 $\times$ 10 ³	*	3.18
Ethylene glycol	47.7	21.81	33.5 $\pm$ 0.5	1.445	2.18 $\times$ 10 ³	*	2.96

* The value is not a constant, it can be varied anywhere from sub-atomic dimensions to unreasonably large order of magnitude

Figure 4.12. Combined molecular hydrodynamic model fitting for receding data of simple liquids

Table 4.9. Combined molecular-hydrodynamic model parameters for receding data of simple liquids

Liquid	Surface Tension (mN/m)	Viscosity (Cp)	Equilibrium Contact angle	λ (nm)	K_w (sec ⁻¹)	L_s (mm)	L (mm)
Water	72.8	0.995	54.1 ± 1.1	0.386 ± 0.205	1.069 ± 0.027 × 10 ⁶	* 1.028 × 10 ²⁵	3.85
Glycerin	65.2	924.27	46.0 ± 1.5	1.147 ± 0.284	6.55 ± 1.06 × 10 ³	3.25	3.25
Formamide	58.2	3.81	30.5 ± 2.0	0.614 ± 0.21	1.235 ± 1.22 × 10 ⁶	3.24	3.24
Ethylene glycol + 30% water	53.4	8.66	36.5 ± 0.5	1.555 ± 0.377	1.0792 ± 0.532 × 10 ⁴	3.18	3.18
Ethylene glycol	47.7	21.81	33.5 ± 0.5	1.788 ± 0.471	8.251 ± 1.087 × 10 ³	2.96	2.96

* The value is not a constant, it can be varied anywhere from sub-atomic dimensions to unreasonably large order of magnitude

Figure 4.13. Combined molecular-hydrodynamic model fitting for advancing data of PDMS oils

Table 4.10. Combined molecular-hydrodynamic model parameters for advancing data of PDMS oils

PDMS oil viscosity (cSt)	Surface tension (mN/m)	Equilibrium contact angle (°)	λ (nm)	$K_w(\text{sec}^{-1})$	Capillary length, L (m)	Slip length, L_s (m)
100	20.9	49	6.013	2.094×10^{-2}	2.1079×10^{-3}	3.246×10^{-7}
1,000	21.1	51	4.418	12.04	2.1069×10^{-3}	7.254×10^{-8}
10,000	21.1	52	1.755	2.216×10^3	2.1037×10^{-3}	8.529×10^{-7}
60,000	21.1	52	1.2067	1.7697×10^3	2.1037×10^{-3}	4.315×10^{-5}

Figure 4.14. Combined molecular-hydrodynamic model for receding data of PDMS oils

Table 4.11. Combined molecular-hydrodynamic model for receding data of PDMS oils

PDMS Oil Viscosity (cSt)	Surface Tension (mN/m)	Equilibrium contact angle (°)	λ (nm)	K_w (sec ⁻¹)	Capillary length, L (m)	Slip length, L _s (m)
100	20.9	49	9.473	2.224×10^2	2.1079×10^{-3}	7.239×10^{-9}
1,000	21.1	51	9.703	2.121×10^{-3}	2.1069×10^{-3}	1.707×10^{-8}

Figure 4.15. Contact angle hysteresis change with speed for simple liquids

Figure 4.16. Contact angle hysteresis for PDMS oils (a) change with speed (b) change with viscosity

CONCLUSIONS

The dynamic wetting behavior of simple liquids (water, glycerin, formamide, ethylene glycol, and mixture of ethylene glycol and water) on bare glass plates has been successfully quantified by measuring the advancing and receding contact angles over a wide range of velocities (0.1 mm/min - 300 mm/min). The viscosity effect on dynamic wetting is investigated through measuring contact angles of polydimethylsiloxane (PDMS) oils with different viscosities (5 cSt - 60,000 cSt) on fluoropolymer coated glass plates. Three theoretical models, hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic, are compared with experimental results, and the significance of models' fitted parameters are discussed.

The hydrodynamic model does not explain the experimentally observed dependence of dynamic contact angles of simple liquids on the contacting velocity. The main drawbacks are: the model does not explain the plateau region and that the fitted L_s values are not physically meaningful (in the subatomic dimension). The molecular-kinetic model describes the change in dynamic contact angles with speed for simple liquids, and the parameters, λ and K_w , are in accordance with the other systems observed in the literature. However, the fitted values of λ and K_w are significantly different in advancing and receding cases. This inconsistency in the advancing and receding cases questions the assumption in the molecular-kinetic model that "the same amount of work is done on each site, irrespective of whether the adsorption site is occupied by the

advancing phase or the receding phase”.²⁸ The combined molecular-hydrodynamic model does not make a significant difference when compared to the fitting of the molecular-kinetic model for the simple liquids, which contradicts with Petrov et al.’s conclusion that the molecular-kinetic model gives the best fit for simple liquids.^{15,27} In this work, the parameters λ and K_w , from the combined model, are similar to the values from the molecular kinetic model, but the hydrodynamic parameter, L_s , from the combined model is physically unreasonable for all the simple liquids. The dominance of molecular-kinetic parameters in the combined model suggests that the molecular displacement (adsorption and desorption) process at the three phase contact line may be dominant for the simple liquids observed in this study.

The present work provides the first, to the best of knowledge, extensive comparison of all three theoretical models with a wide range (5 cSt - 60,000 cSt) of viscosity data. The hydrodynamic model fits well with the dynamic contact angle data of PDMS oils with different viscosities in terms of their linear relationships (θ^3 versus V), but the fitted equilibrium contact angles are significantly different from the measured values, and the slip length values are several orders of magnitude larger than the molecular dimensions. This study observed a low limit (in the order of 10^{-3}) and a possible high limit in terms of capillary numbers to apply the hydrodynamic model. Due to the uncertainties about the appropriate “cut-off” limit for L_s values, the exact upper limit is not presented. The molecular-kinetic model provides a relatively poor fitting to the experimental data of PDMS oils, although it does suggest that the K_w value decreases with increasing viscosity, which leads to the possibility that high viscosities slow down

the quasi-equilibrium rate of wetting. The combined model fits reasonably well in terms of the curve fitting and the magnitude of the inner region (L_s) seems to increase with the increasing viscosity of the oils. However, the fitted parameter K_w values are not practically meaningful in some cases and they do not follow a reasonable trend (K_w is increasing with viscosity of the oil).

Ultimately, this work indicates that the dynamic wetting behavior is a multi mechanism process and none of the tested models, specifically, the hydrodynamic, molecular-kinetic and combined models is sufficient to completely interpret the experimental data for the systems investigated.

The contact angle hysteresis of the simple liquids and PDMS oils has also been investigated. This work strongly supports the hypothesis that the hysteresis depends on the interactions between contacting fluids and the solid substrates.³⁰ This work also provides the evidence that the contact angle hysteresis is also a strong function of the viscosity of contacting fluid.

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APPENDIX A

The following plots show the raw data of force versus distance from which the contact angle at each point has been calculated. The contact angles in this work have been taken by adjusting the slope of the force curve, either linearly decreasing (advancing) or linearly increasing (receding). The intercept is considered as the net force ($F-F_b$) in equation 3.1.

Figure A.1. Comparison of raw (Force) data for PDMS oils with different viscosities at the contact speed of 1 mm/min

Table A.1. Comparison of slopes and intercepts for PDMS oils (data from Figure A.1.)

Viscosity	Slope		Intercept	
	Advancing	Receding	Advancing	receding
5 cSt	-0.0389	-0.0403	0.6134	0.7077
100 cSt	-0.0413	-0.044	0.5407	0.6816
1,000 cSt	-0.0436	-0.0454	0.4969	0.72
5,000 cSt	-0.0425	-0.0282	0.3025	0.9226
10,000 cst	-0.0451	-0.0659	0.3169	1.1939
60,000 cSt	-0.0613	-0.0881	0.1294	2.0017

Figure A.2. Comparison of raw (Force) data for PDMS oils with different viscosities at the contact speed of 300 mm/min

Table A.2. Comparison of slopes and intercepts for PDMS oils (data from Figure A.2.)

Viscosity	Slope		Intercept	
	Advancing	Receding	Advancing	Receding
5 cSt	-0.041	-0.0418	0.6519	0.6901
100 cSt	-0.0621	-0.0942	0.1651	1.4668
1,000 cSt	-0.1628	-0.2203	-0.4048	3.6483
5,000 cSt	-0.5909	-0.2498	-0.8344	9.3123
10,000 cSt	-0.9288	-0.3867	-0.8769	11.975
60,000 cSt	-2.9863	0.1279	-1.1956	35.91

The following plots show the comparison of contact angles at different distances on the glass plate for PDMS oils with different viscosities. The contact angles at each point have been calculated using equation 3.1.

Figure A.3. Contact angles of PDMS oils at each point on the glass plate at the contact speed of 1 mm/min

Figure A.4. Contact angles of PDMS oils at each point on the glass plate at the contact speed of 300 mm/min

APPENDIX B

The goodness of fit of all the three models, hydrodynamic, molecular-kinetic model, and combined molecular-hydrodynamic model has been investigated for each liquid observed in the present study.

Simple liquids

Since the hydrodynamic model for simple liquids does not explain the velocity dependence of dynamic contact angle in the entire observed velocity region, the goodness of fit of this model for the simple liquids data is not calculated. The goodness of fit values of molecular-kinetic model and combined molecular-hydrodynamic model have been compared for each liquid in Table B.1 and Table B.2 for advancing and receding cases, respectively. The sum of the squares of the differences between calculated and measured values of contact angles is calculated for each liquid. This sum is similar for molecular-kinetic and combined molecular-hydrodynamic models for all the simple liquids, except glycerin.

PDMS oils

The goodness of fit of all three models for PDMS oils with different viscosities have been compared in Table B.3. Since the receding data of only some of the PDMS oils are fitted with models, the goodness of fit for receding case is not presented here. The some of the squares of the errors are randomly varying for different models. Overall, the combined model gives reasonable values for sums of the squares of the errors for most of the PDMS oils.

Table B.1. Comparison of goodness of fit of molecular-kinetic, and combined models for advancing data of Simple liquids

Liquid	Sum of the square of the error (χ^2)	
	Molecular-kinetic model	Combined model
Water	269.8593	269.4302
Glycerin	79.69926	36.79016
Formamide	110.7755	107.7711
Ethylene Glycol (70%) + Water (30%)	187.2896	202.7801
Ethylene Glycol	40.80362	39.30426

Table B.2. Comparison of goodness of fit of molecular-kinetic and combined models for receding data of Simple liquids

Liquid	Sum of the square of the error (χ^2)	
	Molecular-kinetic model	Combined model
Water	17.69444	23.55839
Glycerin	113.1603	113.1604
Formamide	103.8703	103.8703
Ethylene Glycol (70%) + Water (30%)	68.10624	38.63401
Ethylene Glycol	20.51486	28.34689

Table B.3. Comparison of goodness of fit of hydrodynamic, molecular-kinetic, and combined models for advancing data of PDMS oils

Viscosity of the PDMS oil	Sum of the square of the error (χ^2)		
	Hydrodynamic model	Molecular-kinetic model	Combined model
5 cSt	753.6256	807.0766	121.4863
100 cSt	36.30593	237.8427	14.57089
1,000 cSt	78.80388	136.6255	7.99544
10,000 cSt	152.6340191	23.61061	5.618271
60,000 cSt	19.29634	607.8923	29.0978

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