

Dynamic wetting: Hydrodynamic or molecular-kinetic?

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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 the models' adequacy. Our work suggests that the molecular displacement, i.e., the adsorption and desorption process, seems to be dominant for the simple liquids investigated. For polydimethylsiloxanes, our work suggests that none of the evaluated models is sufficient to explain the experimentally observed dependence of the dynamic contact angle on contact velocity. This work, to the best of our knowledge, provides the first extensive comparison of the three models with experimental data over a wide range of viscosity. In addition, we have investigated the contact angle hysteresis and conclude that it is a strong function of the contact speed, the interactions between the fluids and the substrate, and the fluid viscosity.

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1. Introduction

Wetting and dewetting are “ubiquitous in natural and industrial processes” [1]. The fundamentals of equilibrium wetting phenomenon have been well explored [2–10]; however, the dynamic process, which is particularly important for many practical applications, remains poorly understood. For example, when a moving liquid is in contact with a solid substrate, there are two controversial models, hydrodynamic and molecular-kinetic, that interpret the dynamic wetting/dewetting process. The hydrodynamic model, developed by Cox [11] and Voinov [12], considers the process to be dominated by the viscous dissipation of the liquid, assuming the bulk viscous friction is the main resistance force for the three-phase contact line motion. The model separates the liquid into an inner region and an outer region [13], sometimes even with an intermediate region. In the outer region, the “no-slip” boundary of classical hydrodynamics (viscous dissipation is the dominant force) is applied, whereas in the

inner region, it is assumed that the slippage of fluids occurs within the first couple of layers of molecules adjacent to the solid surface. The relationship between velocity (V) and dynamic contact angle (θ^d) is given by [14]

$$(\theta^d)^3 = (\theta^0)^3 \pm 9 \frac{\eta V}{\gamma_{lv}} \ln \left(\frac{L}{L_s} \right), \quad (1)$$

where θ^0 is the equilibrium contact angle, η is the viscosity of the liquid, γ_{lv} is the surface tension of the liquid, L is the characteristic capillary length, and L_s is the slip length. In Eq. (1), the plus sign applies to the advancing liquid movement and the minus sign applies to the receding liquid movement. The capillary length, L , is given by $L = \sqrt{(2\gamma_{lv}/\rho g)}$, where ρ is the density of the liquid [14]. The slip length, L_s , is the fitting parameter and represents the length of the region where the no-slip boundary condition of classical continuum theory does not hold (i.e., the first couple of layers of molecules adjacent to the solid surface), thus the value of L_s should be in the order of molecular dimensions [11,15]. It is worthwhile to note that the hydrodynamic model does not take into account the characteristics of the solid surface, which is the model's main limitation.

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In contrast to the hydrodynamic model, the molecular-kinetic model excludes the viscous dissipation and takes the solid surface characteristics into account [16,17]. The molecular-kinetic model, which is based on Eyring's statistical treatment of the transport process [18,19], assumes that the energy dissipation occurs only at the moving contact line following the adsorption and desorption process and that the entire interface follows the Laplace equation. The relationship between dynamic contact angle and velocity is given by [14,20,21]

$$\cos \theta^d = \cos \theta^0 \mp \frac{2kT}{\gamma_V \lambda^2} \operatorname{arcsinh} \left(\frac{V}{2K_w \lambda} \right), \quad (2)$$

where k is the Boltzman constant, T is the temperature, and λ and K_w are the fitting parameters. The parameter λ is the distance between two adsorption or desorption sites, and K_w is the quasi-equilibrium rate constant. The negative and positive signs apply to the advancing and receding cases, respectively. The molecular-kinetic model takes into account the characteristics of the solid surface reflected by the adsorption and desorption sites. The expected values for λ and K_w are in the order of molecular dimension, 1 nm and 10^6 s^{-1} , respectively, from curve fitting experimental data [14]. These values are reasonable in terms of the average length of molecular displacement and the adsorption/desorption rate.

It is clear that the hydrodynamic model and molecular-kinetic model are two contradicting explanations for the dynamic wetting and dewetting processes, and that in many instances neither model fits the entire velocity range of experimental data [14,22,23]. Thus, a combined molecular-hydrodynamic approach has been proposed [24,25], which assumes that the equilibrium contact angles have a strong dependence on velocity. By replacing the equilibrium contact angle in Eq. (1) with the $\arccos \theta^d$, where θ^d is in Eq. (2), the dynamic contact angle dependence on contact line velocity is given by [25]

$$(\theta^d)^3 = \left\{ \arccos \left[\cos \theta^0 \mp (2kT/\gamma_V \lambda^2) \operatorname{arcsinh}(V/2K_w \lambda) \right] \right\}^3 \pm (9\eta V/\gamma_V) \ln(L/L_s), \quad (3)$$

where λ , K_w , and L_s are the fitting parameters; all the constants and parameters in Eq. (3) represent the same parameters and the same expected values as discussed in the hydrodynamic and molecular-kinetic models.

There are controversies over the applicability of theoretical models to experimental dynamic contact angle data and in relating the model parameters to solid/liquid properties. Cox [11] compared his hydrodynamic model to the experimental data of a glass/silicone oils/air system performed by Hoffman [26] and found that the results were in good agreement with the hydrodynamic model (Eq. (1)) over the observed velocity region. On the other hand, the dynamic contact angles of water and glycerol on a polyethylene terephthalate (PET) surface show that the hydrodynamic model fits well only with a limited velocity range (the medium

range) [27]. This contradicts the work by Redon et al. [28] on silicone oils over silicon wafers which leads to the conclusion that the hydrodynamic theory works well at low contact velocities.

Blake and Haynes measured the dynamic wetting of a water/benzene interface along a capillary tube and compared it with their developed molecular-kinetic model [16]. The results were in good agreement with their theoretical predictions. Later on, Blake reported a multi-mechanism behavior over a wide range of velocities (3.16×10^{-5} – 10 m/s) for a PET/water/air system [21]. The molecular-kinetic model gives two different sets of parameters (λ and K_w) for very high and very low velocities. For intermediate velocities, a stick-slip movement of the three-phase contact line was observed [21]. Blake hypothesizes that the multi-mechanism is likely due to the variation of solid/liquid interaction when the contact speed changes. Petrov and Petrov conducted experiments on the PET/aqueous glycerol solutions/air system over a low velocity region (10^{-3} – 2 mm/s) and also obtained two different sets of parameters within this region using the molecular-kinetic model [29]. However, Hayes and Ralston [27] were able to fit their experimental data of a PET/aqueous glycerol/air system with the molecular-kinetic model with a physically reasonable single set of parameters [27].

Recently, the success of the combined molecular-hydrodynamic approach has been reported by Schneemilch et al. [14] by comparing the experimental dynamic contact angles of octamethylcyclotetrasiloxane (OMCTS) on low energy fluoropolymer surfaces with the hydrodynamic, molecular-kinetic, and combined molecular-hydrodynamic models. Neither the hydrodynamic nor the molecular-kinetic model fits the data over the entire velocity range, but the combined molecular-hydrodynamic model does. Similar observations were also made with hexadecane [14]; however, it is worthwhile to note that in both cases, the fitted L_s values from the combined models are significantly larger than the molecular dimensions of hexadecane and OMCTS [14].

Another fundamental question that remains unclear is about the contact angle hysteresis. Contact angle hysteresis is the difference between advancing and receding contact angles, and is often referred to as the measure of roughness and/or heterogeneity of the solid substrate. Recently, Extrand concluded that, in some cases, the effect of liquid/substrate interactions is a stronger contribution factor to the contact angle hysteresis than surface roughness [30,31]. This conclusion was generated by quantifying the contact angle hysteresis of several organic liquids on polymer and silicon surfaces [30,31]. It has also been reported that the hysteresis is related to a stick-slip mechanism which depends on the disorder and the size of the system [32].

In this work, we report a systematic investigation of dynamic wetting on different systems, specifically, simple liquids and polydimethylsiloxane (PDMS) oils with different viscosities. We have compared the experimental data with the hydrodynamic, molecular-kinetic, and combined

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