

## Chapter 2

# Experimental Study on the Nanofluid Dynamic Wetting

**Abstract** In this chapter, the time-dependent wetting radius and contact angle for various nanofluid droplets were measured to study the dynamic wetting behaviors of nanofluids. The experiment results show that the adding of nanoparticles inhibits the dynamic wetting of nanofluids as compared with base fluids. The reduced spreading rate can be attributed to the increase in either surface tension or viscosity due to adding nanoparticles into the base fluid. Once the effects of the surfaces tension and viscosity are both eliminated using the non-dimensional analysis, the wetting radius versus spreading time curves for all the nanofluid droplets overlap with each other. The spreading exponent fitted from the nanofluid dynamic wetting data agrees with the prediction of the classical hydrodynamics model derived from the bulk viscous dissipation approach. The present study proves that the spreading of the nanofluid droplets is dominated by the bulk dissipation rather than by the local dissipation at the moving contact line.

## 2.1 Introduction

The attractive and tunable wetting behaviors extend the applications of nanofluids into many scientific and engineering areas; however, the mechanisms of nanofluid dynamic wetting are not well understood [1–6]. Many parameters may be controlled in nanofluids, such as the nanoparticle material, size, shape, and loading, as well as base fluid material. By changing nanoparticles or base fluid, nanofluids exhibit enhanced [3] or reduced [7] thermal conductivity, increased [8, 9] or decreased [10] surface tension, as well as shear-thinning [11] or shear-thickening [12] rheological properties. It can be expected that when nanofluid droplets spread on a solid surface, they will also show different dynamic wetting behaviors. The expectation has been confirmed by the recent reports [13–18]. Wang et al. [13, 14] compared experimentally the spreading behaviors of pure poly (propylene glycol, PPG) and PPG+10 nm silica nanofluids. Their results showed that the wetting radius versus time relation ( $R - t$ ) and the dynamic contact angle versus contact line

velocity relation ( $\theta_D - U$ ) for the pure PPG followed the Newtonian spreading laws; however, the  $R - t$  and  $\theta_D - U$  relations for the PPG+ silica nanofluids significantly deviated from the Newtonian spreading laws. The deviations were attributed to the fact that adding silica nanoparticles into the solvent led to a shear-thickening rheology. However, a distinct dynamic wetting behavior for nanofluids was reported by Wasan et al. [15–18]. They presented that 8 nm micellar solution and 20-nm silica suspension significantly enhanced the spreading rate as compared with their base fluids. A solid-like ordering structure of nanoparticles was observed near the contact line region using interferometry [15]. Thus, the super-spreading was explained by the structural disjoining pressure due to the self-assembly of nanoparticles in the vicinity of the contact line [15–18]. The super-spreading behavior of nanofluids has been widely used to explain the enhanced drop-wise evaporation [19, 20] and the elevated critical heat flux with nanofluids [21–24]. Another explanation for the super-spreading by nanofluids was that nanoparticles were assumed to settle at the bottom of the droplet, thus reducing the solid–liquid friction and hence facilitating the fluid spreading [25].

The previous studies [13–18] dealt with dynamic wetting behaviors of nanofluids with high nanoparticles fraction. However, high fraction nanofluids are unstable due to the nanoparticle sedimentation, which has become a serious challenge for potential applications of nanofluids. Thus, it is indeed necessary to investigate dynamic wetting characteristics of dilute nanofluids. Recently, Liang et al. [26] proposed that the timescale for the nanoparticles diffusing from the bulk droplet to the contact line region is far larger than that for the droplet spreading, so that the nanoparticle fraction in the contact line region is actually lower than the nominal fraction of bulk droplet. As a result, the shear-thickening nanofluids behave like quasi-Newtonian spreading characteristics. The limited diffusion rate of the nanoparticles was also confirmed for the spreading of gold–water nanofluids on a gold surface via molecular dynamic simulations [27]. For the dilute nanofluids, nanoparticles are harder to diffuse to the contact line region; thus, the super-spreading and shear-thickening spreading may not occur. Unfortunately, the dynamic wetting for the dilute nanofluids has not been reported up to now.

The relations of  $\theta_D - U$  and  $R - t$  are usually used to describe the dynamic wetting of fluids on solid surfaces. These two relations not only present the wettability of the fluids on the solid surfaces, but also show the energy dissipation mechanisms during the dynamic wetting process [28–31]. Unfortunately, few studies focus on measurements of  $\theta_D - U$  and  $R - t$  for nanofluids. Without  $\theta_D - U$  and  $R - t$  experimental data, the dynamic behaviors cannot be accurately described.

This chapter investigates dynamic wetting behaviors of dilute nanofluids by measuring  $\theta_D - U$  and  $R - t$  data using the droplet spreading method. The effects of nanoparticle material, diameter, and loading, as well as base fluid and substrate material, were examined. The purpose of this work is to reach the following two targets. The first is to answer whether the super-spreading and/or shear-thickening spreading behaviors will also be observed for dilute nanofluids. The second is to address how nanoparticles affect dynamic wetting behaviors in dilute nanofluids, if the two behaviors do not occur.

## 2.2 Experimental Methods

### 2.2.1 Experimental Setup

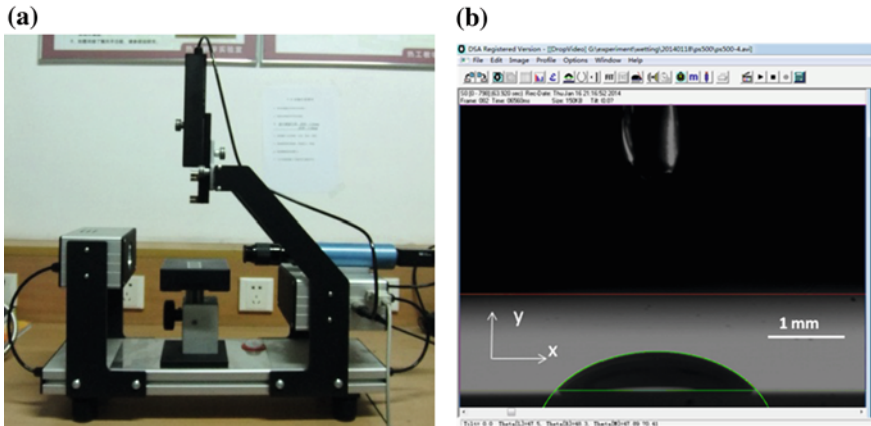
The  $\theta_D$ - $U$  and  $R$ - $t$  data were first measured using a drop shape analyzer (EasyDrop FM40, Krüss GmbH, Hamburg, Germany), as shown in Fig. 2.1a. The spreading process was recorded by a high-speed CCD camera at 60 frames per second. The contact angle and the spreading radius were measured by fitting the droplet profile with the equation  $y = a + bx + cx^{0.5} + d/\ln x + e/x^2$  for each picture as shown in Fig. 2.1b. The standard error in the contact angle measurement was  $\pm 1^\circ$ . The contact line velocity was calculated using  $U = df(t)/dt$ , where  $f(t)$  was fit from the  $R$ - $t$  curves.

The surface tension and the  $\theta_D$ - $U$  curves were then measured using Krüss K100 MK2 (Krüss GmbH, Hamburg, Germany) based on the Wilhelmy plate method, as shown in Fig. 2.2. The substrate was inserted into the liquid reservoir at various velocities. As shown in Fig. 2.2b, the forces imposed on the plate are as follows:

$$F = L \cdot \sigma \cdot \cos \theta_D - \rho g S h, \quad (2.1)$$

where  $L$  is the wetting perimeter,  $\rho$  is the liquid density,  $S$  is the cross-sectional area of the plate,  $h$  is the inserted distance, and  $\gamma$  is the liquid-vapor surface tension. The measured  $F$ - $h$  curves had good linearity as shown in Fig. 2.2b with the contact angle and then the contact angle is calculated as follows:

$$\theta_D = \arccos\left(\frac{F_0}{L \cdot \sigma}\right), \quad (2.2)$$



**Fig. 2.1** Droplet spreading method: **a** Krüss EasyDrop; **b** Contact angle and spreading radii based on image analysis

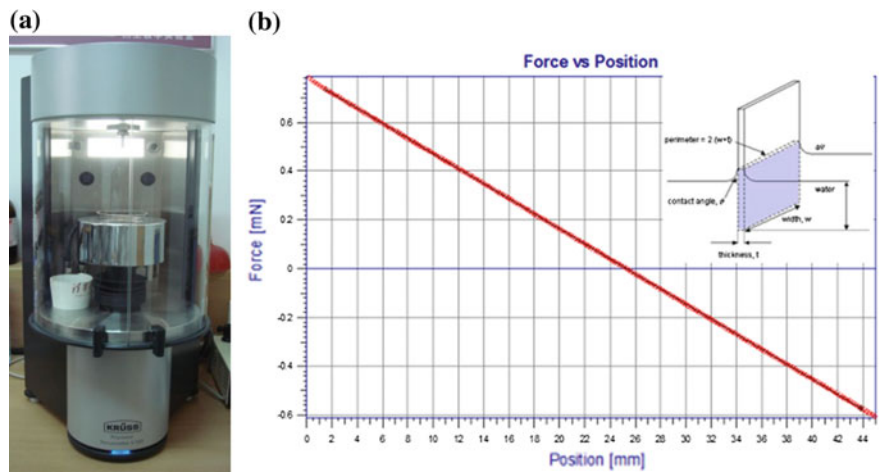


Fig. 2.2 Wilhelmy plate method: **a** Krüss K100 MK2; **b** schematic

Table 2.1 Experimental capacities

Measurement	Method	Company	Type	Capability
$R - t, \theta_D - U$	Droplet spreading	Krüss	Krüss FM40 EasyDrop Standard	Resolution: 0.1°; Highest capture spread: 60 frames/s
$\sigma, \theta_D - U$	Wilhelmy plate	Krüss	Krüss K100 MK2	Max insert: 110 mm; resolution: 0.1 $\mu\text{m}$ ; Velocity range: 0.09–500 $\text{mm min}^{-1}$

where  $F_0$  is the intercept in Fig. 2.2b. The surface tension was also measured by a Krüss K100 MK2 using a platinum plate.

The accuracies of the experimental setups are listed in Table 2.1.

2.2.2 Nanofluid Preparation

The measurements of the nanofluid dynamic wetting characteristics required stable nanofluids and clean substrates and beakers. Hence, all the substrates (glass slides, mica slides, and silicon wafers) and the beakers were cleaned with ethanol solution with more than 30-min ultrasonic cleaning. The ultrasonic cleaning procedure was then repeated with acetone and then with the deionized water.

As shown in Table 2.2, the study considered the effects of various nanofluid parameters on the dynamic wetting, including the nanoparticle loading ( $\text{SiO}_2/\text{PDMS500}$  (polydimethylsiloxane, viscosity of 100 mPa s),  $d = 20$  nm,  $\varphi = 0, 0.5, 1$ , and 2 %), nanoparticle material ( $\text{SiO}_2, \text{TiO}_2, \text{Al}_2\text{O}_3/\text{PDMS500}$ ,  $d = 20$  nm,

**Table 2.2** Nanofluid parameters used for the dynamic wetting tests

Effects	Materials <sup>a</sup>	Diameter (nm)	Base fluids <sup>a</sup>	Loadings (%)	Substrates
Loadings	SiO <sub>2</sub>	20	PDMS500	0.5	Glass
	SiO <sub>2</sub>	20	PDMS500	1	Glass
	SiO <sub>2</sub>	20	PDMS500	2	Glass
Diameters	SiO <sub>2</sub>	10	PDMS500	1	Glass
	SiO <sub>2</sub>	15	PDMS500	1	Glass
	SiO <sub>2</sub>	20	PDMS500	1	Glass
Materials	SiO <sub>2</sub>	20	PDMS500	1	Glass
	TiO <sub>2</sub>	20	PDMS500	1	Glass
	Al <sub>2</sub> O <sub>3</sub>	20	PDMS500	1	Glass
Base fluids	SiO <sub>2</sub>	10	PDMS100	1	Glass
	SiO <sub>2</sub>	10	PDMS500	1	Glass
	SiO <sub>2</sub>	10	PDMS1000	1	Glass
	SiO <sub>2</sub>	10	PEG200	1	Glass
	SiO <sub>2</sub>	10	PEG400	1	Glass
Substrates	SiO <sub>2</sub>	20	PDMS500	1	Glass <sup>b</sup>
	SiO <sub>2</sub>	20	PDMS500	1	Mica <sup>c</sup>
	SiO <sub>2</sub>	20	PDMS500	1	Silicon wafer <sup>d</sup>

<sup>a</sup>Sigma-Aldrich Co., <sup>b</sup>Fisher Co., <sup>c</sup>SPI Supplies, and <sup>d</sup>UMCO

**Table 2.3** Nanoparticle properties

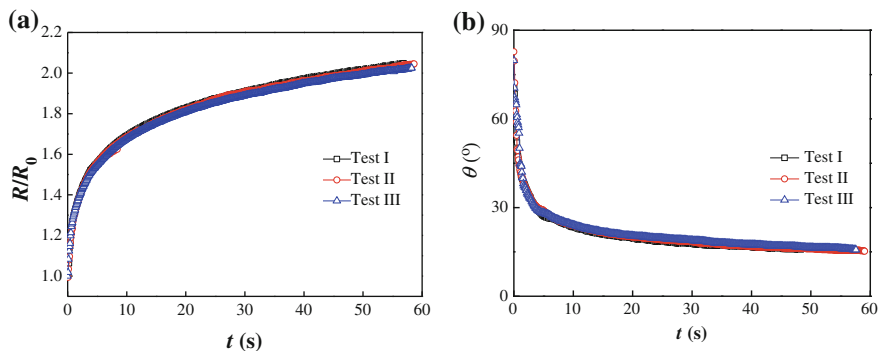
Properties	SiO <sub>2</sub>	SiO <sub>2</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Wettability	Hydrophilic				
BET (m <sup>2</sup> /g)	90 ± 15	130 ± 25	150 ± 15	50 ± 15	100 ± 15
Diameter (nm)	10 ± 1	15 ± 1	20 ± 1	20 ± 1	20 ± 1
Density (g/l)	50–120	50–120	50–120	–100	–80

$\phi = 1\%$ ), nanoparticle diameter (SiO<sub>2</sub>/PDMS500,  $\phi = 1\%$ ,  $d = 10, 15$ , and  $20$  nm), and base fluid (SiO<sub>2</sub>/PDMS100, PDMS500, PDMS1000, PEG200 (polyethylene glycol, molecular weight of  $200$  g/mol), PEG4000,  $d = 20$  nm,  $\phi = 1\%$ ). All the nanoparticles (SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>) and base fluids (PDMS100, PDMS500, PDMS1000, PEG200, and PEG4000) were Sigma-Aldrich products.

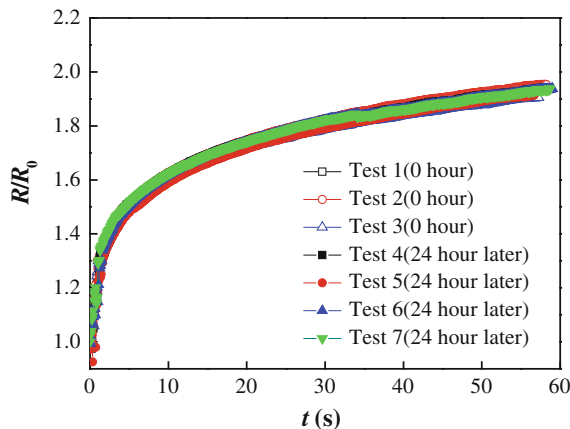
Stable nanofluids were obtained by mixing all the nanofluid suspensions in the ultrasonic cleaner for more than  $12$  h. The nanofluids were observed to be stable for  $48$  h. All the measurements were conducted within  $1$  or  $2$  h after the nanofluids were prepared. In addition, the dynamic wetting attests to a small droplet lasts only several minutes, which is much shorter than the nanofluid stability time. Hence, the nanofluid stability had no effect on the dynamic wetting experiments. All the tested nanofluid parameters and substrates are listed in Table 2.3.

### 2.2.3 Experiment Repeatability and Reliability

The repeatability and reliability of experimental method are illustrated by the details shown in Figs. 2.3, 2.4, and 2.5. Figure 2.3 shows the spreading radius (Fig. 2.3a) and the dynamic contact angle (Fig. 2.3b) evolution for three tests with the same PDMS500 liquid within 1 h after the fluid was prepared. Both the spreading radius and the dynamic contact angle evolution curves almost overlap, indicating the repeatability and reliability of the experimental method. Figure 2.4 shows seven

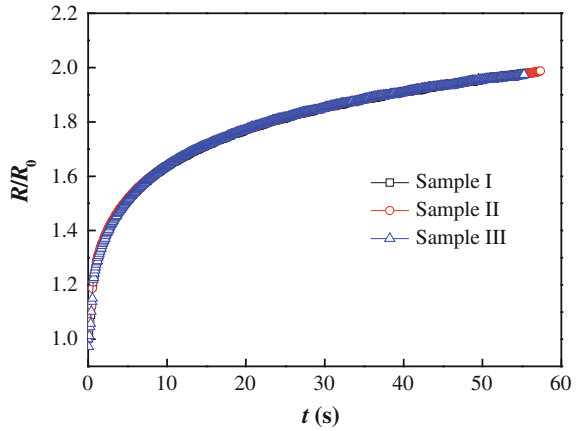


**Fig. 2.3** Experiment repeatability testing: three measurements of **a** spreading radius versus time and **b** dynamic contact angle evolutions for the same PDMS500 liquid within 1 h



**Fig. 2.4** Seven measurements of spreading radius evolution for the same  $\text{SiO}_2/\text{PDMS500}$  nanofluids ( $d = 20$  nm,  $\varphi = 0.5$  %): Test Nos. 1–3 were measured immediately when the nanofluids were well prepared; Test Nos. 4–7 were measured after 24 h when the nanofluids were prepared

**Fig. 2.5** Dynamic wetting measurements of  $\text{Al}_2\text{O}_3/\text{PDMS500}$  nanofluids ( $d = 20$  nm,  $\phi = 0.5$  %) which were prepared at different times



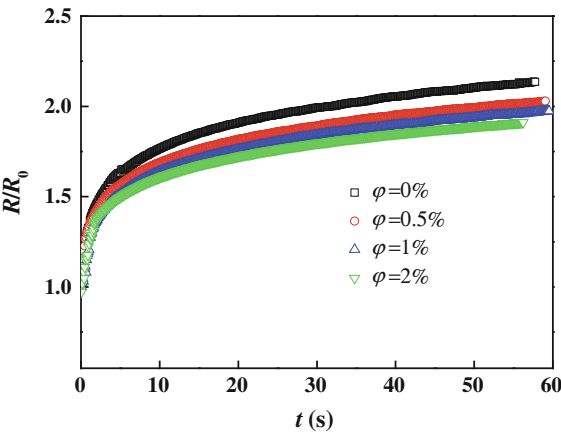
measurements for the same  $\text{SiO}_2/\text{PDMS500}$  nanofluid ( $d = 20$  nm,  $\phi = 0.5$  %), in which Test Nos. 1–3 were measured immediately when the nanofluids were prepared, while Test Nos. 4–7 were measured 24 h after the nanofluids were prepared. The consistent results show the good stability of the nanofluids. Figure 2.5 shows the dynamic wetting characteristics of  $\text{Al}_2\text{O}_3/\text{PDMS500}$  nanofluids ( $d = 20$  nm,  $\phi = 0.5$  %) prepared at different times. The overlapping curves show the repeatability of the nanofluid preparation method.

## 2.3 Results and Discussions

### 2.3.1 Spreading Behavior of Dilute Nanofluids

Figure 2.6 shows the evolution of the spreading radius for  $\text{SiO}_2/\text{PDMS500}$  nanofluid droplets with various nanoparticle loadings ( $\phi = 0, 0.5, 1$ , and  $2$  %) on the glass slide. Here,  $R_0$  denotes the droplet radius prior to spreading. Since glass slides, mica slides, and silicon wafers are high-energy surfaces, the nanofluid droplets studied in this work were found to spread completely to a thin film on these surfaces. Consequently, the initial radius,  $R_0$ , was used for the non-dimensional analysis. Compared with the base fluid ( $\phi = 0$ ), adding nanoparticles inhibits rather than facilitates the dynamic wetting for the three nanoparticle loadings ( $\phi = 0.5, 1$ , and  $2$  %). The spreading rate and the spreading area decrease with increasing nanoparticle loadings, for example,  $R/R_0 = 2.10$  for PDMS500 ( $\phi = 0$ ) at  $t = 50$  s, while  $R/R_0 = 1.99$  for  $\phi = 0.5$  %,  $R/R_0 = 1.93$  for  $\phi = 1$  %, and  $R/R_0 = 1.89$  for  $\phi = 2$  %. The reduced spreading speed and the equilibrium wetting radius were also reported for the impinging of a liquid drop with micron-sized particles on surfaces [32]. For the micron-sized particles, the sedimentation of particles takes place more easily. Thus, an annular particle distribution was observed for higher impinging

**Fig. 2.6** Effects of nanoparticle loadings on the dynamic wetting of nanofluids (SiO<sub>2</sub>, PDMS500,  $\varphi = 0, 0.5, 1$ , and  $2\%$ ,  $d = 20\text{ nm}$ )



velocities, and the periphery of the drop was always depleted of particles owing to interfacial forces acting on the particles [32]. However, these phenomena do not occur for the spreading of dilute nanofluids.

**2.3.2 Individual Parameter Analysis of Nanofluid Dynamic Wetting**

To perform the individual parameter analysis, the nanofluids were divided into two groups. One group has different viscosities, while the surface tensions are the same (base fluids: PDMS100, PDMS500, and PDMS1000, nanoparticles: SiO<sub>2</sub> with  $\varphi = 1\%$  and  $d = 10\text{ nm}$ ); the other has different surface tensions, while the viscosities are almost the same (base fluids: PDMS100, PEG200, and PEG400, nanoparticles: SiO<sub>2</sub> with  $\varphi = 1\%$  and  $d = 10\text{ nm}$ ). Therefore, the effects of viscosity and surface tension can be examined individually. The base fluid properties are shown in Table 2.4.

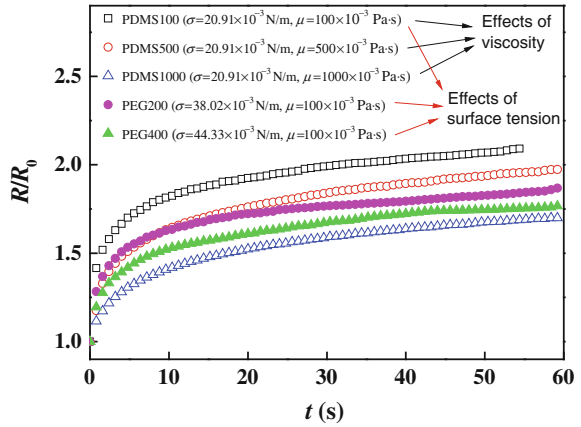
**Table 2.4** Base fluid properties at 20 °C

Base fluids	Density (g/mL)	Surface tension (10 <sup>-3</sup> N/m)	Viscosity (10 <sup>-3</sup> Pa s)
PDMS100 <sup>a</sup>	1.06	20.0	100
PDMS500	0.97	20.0	500
PDMS1000	1.09	20.0	1000
PEG200 <sup>b</sup>	1.12	37.2	108
PEG400	1.12	43.5	120

<sup>a</sup>PDMS100 is polydimethylsiloxane with viscosity of 100 mPa s

<sup>b</sup>PEG200 is polyethylene glycol with molecular weight of 200 g mol<sup>-1</sup>

**Fig. 2.7** Effects of base fluid materials on nanofluids dynamic wetting ( $\text{SiO}_2$ ,  $\varphi = 1\%$ ,  $d = 10\text{ nm}$ )



**Fig. 2.8** The surface tensions of nanofluids ( $\text{SiO}_2$ ,  $d = 10\text{ nm}$ ,  $\varphi = 1\%$ )

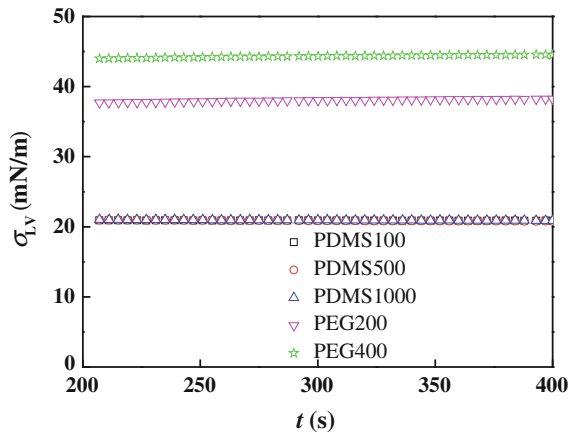
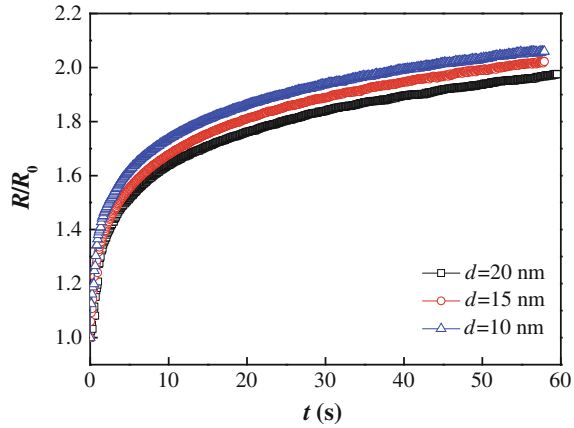


Figure 2.7 shows  $(R/R_0) - t$  curves of the five nanofluids. It is found that the viscosity and surface tension strongly affect the nanofluid dynamic wetting. Both the spreading velocity and the spreading area decrease with increasing viscosity for the three PDMS-based nanofluids. For example,  $R/R_0$  is 2.07 for the PDMS100-nanofluid at  $t = 50\text{ s}$ , while  $R/R_0 = 1.94$  for the PDMS500-nanofluid, and  $R/R_0 = 1.65$  for the PDMS1000-nanofluid. For the nanofluids with the same viscosity (PDMS100-based, PEG200-based, and PEG400-based), the spreading deteriorates with increasing base fluid surface tensions. As shown in Fig. 2.8, the surface tensions of the five nanofluids measured by the Krüss K100 MK2 remain unchanged for a long time (longer than the dynamic spreading process). The surface tension is  $20.91 \pm 0.04\text{ mN m}^{-1}$  for the three PDMS-based nanofluids,  $38.02 \pm 0.05\text{ mN m}^{-1}$  for  $\text{SiO}_2/\text{PEG200}$ , and  $44.33 \pm 0.05\text{ mN m}^{-1}$  for  $\text{SiO}_2/\text{PEG400}$ . The effects of surface tension on the dynamic wetting are explained as follows. The driving force acting on the contact line can be expressed as

**Fig. 2.9** Effects of three nanoparticle diameters on the dynamic wetting ( $\text{SiO}_2/\text{PDMS500}$ ,  $\varphi = 1\%$ ); inserted schematic: non-dimensional radius versus non-dimensional time



$F = \sigma_{\text{SV}} - \sigma_{\text{SL}} - \sigma_{\text{LV}} \cos \theta_{\text{D}}$ , where  $\sigma_{\text{SV}}$  and  $\sigma_{\text{SL}}$  denote the solid–vapor and solid–liquid interfacial tensions, and  $\sigma_{\text{LV}}$  is the liquid–vapor interfacial tension (also referred to as the liquid surface tension). Restated that the nanofluids studied can completely spread on the glass slides, mica slides, and silicon wafers, the dynamic contact angle,  $\theta_{\text{D}}$ , is always smaller  $90^\circ$  in all spreading experiments. Thus, the increase in  $\sigma_{\text{LV}}$  reduces the driving force, which leads to the slower spreading for nanofluids with larger surface tension.

Figure 2.9 shows the effects of the nanoparticle diameter ( $\text{SiO}_2$  with  $d = 10, 15$ , and  $20$  nm, the standard deviation of diameter for each nanoparticle is about  $\pm 1$  nm) on the nanofluid dynamic wetting. The base fluid is PDMS500, and the nanoparticle loading is  $1\%$ . The spreading velocity and spreading area both decrease with increasing nanoparticle diameter. The effects of nanoparticle diameter on the viscosity have been studied experimentally and theoretically [33–36]. These studies demonstrated that increasing the nanoparticle diameter increases the nanofluid viscosity. However, there are no direct evidences to relate the nanoparticle diameter to the surface tension of nanofluids [37–39]. It was reported that the wettability of nanoparticles was responsible for the modified surface tension of nanofluids; adding hydrophilic nanoparticles increases the surface tension of nanofluids, while adding hydrophobic nanoparticles reduces the surface tension [40]. We also measured the surface tensions of nanofluids with the three different nanoparticle diameters. Because the  $\text{SiO}_2$  nanoparticles used are hydrophilic, the surface tensions of the three nanofluids are all higher than that of the base fluid, which agrees with the report in Ref. [40]. The results also show that three nanofluids have the same surface tension, indicating that the nanoparticle diameters do not affect the surface tension of nanofluids. Therefore, Fig. 2.9 again confirms that increasing nanofluid viscosity slows down the spreading of nanofluids.

Based on the individual parameter analysis, it is concluded that the super-spreading behavior does not take place, and the viscosity and surface tension are two dominant parameters for the dynamic spreading of dilute nanofluids.

### 2.3.3 Coupling Effect of Viscosity and Surface Tension

The non-dimensional spreading radius ( $R/R_0$ ) as a function of the coupling parameter,  $t/\mu\sigma_{LV}^2R_0$ , is shown in Fig. 2.10. The use of the coupling parameter is to eliminate the effects of both the surface tension and the viscosity. By eliminating the differences of the surface tension and the viscosity, the original experimental data of  $R/R_0$  versus  $t$  (Fig. 2.7) measured for various nanofluids gather together nearly into a single curve. This result indicates that apart from the viscosity and surface tension, there is no other parameter affecting the dynamic wetting of dilute nanofluids. Therefore, for dilute nanofluids, the role of nanoparticles in the dynamic wetting is realized only through modifying the viscosity and surface tension of nanofluids.

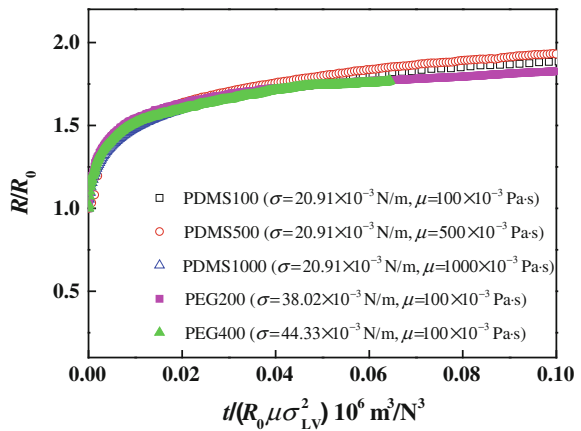
The effects of surface tension and viscosity on the dynamic wetting of dilute nanofluids were further tested by adding three different nanoparticle materials ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$ ) into the same base fluid (PDMS500). The average nanoparticle diameters are 20 nm, and the loadings are 1 % for the three nanoparticle materials. In addition, the three nanoparticles are spherical without any surface treatments. Experimental tests show that three nanofluids have almost the same surface tension and viscosity; thus,  $R/R_0$  versus  $t$  curves are expected to coincide with each other. This is verified by the spreading experiments shown in Fig. 2.11.

### 2.3.4 Mechanisms of Dynamic Wetting in Dilute Nanofluids

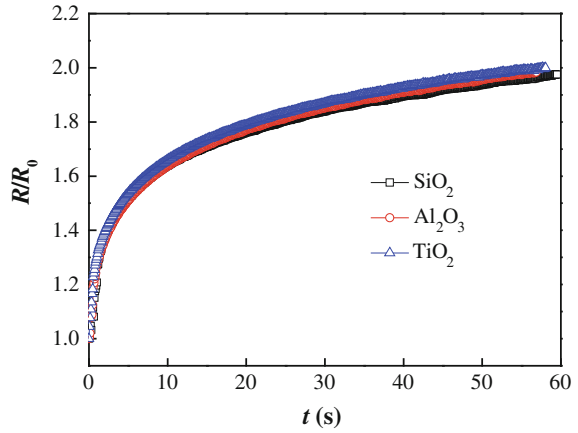
#### 2.3.4.1 Spreading Law of Dilute Nanofluids

The  $R/R_0$ - $t$  data in Fig. 2.6 were replotted in the dual-logarithmic coordinates, as shown in Fig. 2.12. It is found that the new curves for four nanoparticle loadings are all linear ( $R^2 = 0.999$ ). The curves were then fitted by  $R-A t^\alpha$  with the results listed

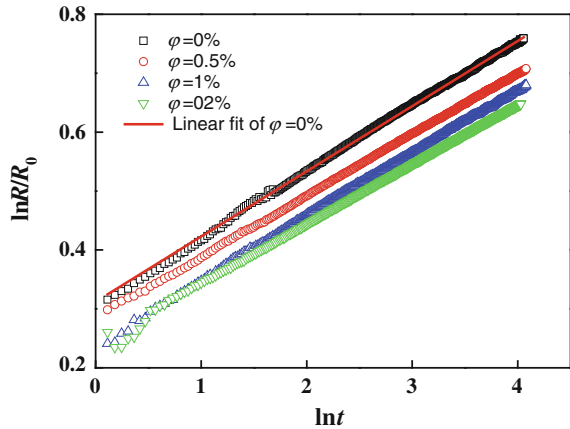
**Fig. 2.10** Effects of surface tension and viscosity on the dynamic wetting of nanofluids using non-dimensional analyzing



**Fig. 2.11** Effects of three nanoparticle materials on the dynamic wetting (PDMS500,  $\varphi = 1\%$ ,  $d = 20\text{ nm}$ )



**Fig. 2.12** Linear fitting in the logarithmic coordinates for nanofluid dynamic wetting with various nanoparticle loadings (SiO<sub>2</sub>, PDMS500,  $\varphi = 0, 0.5, 1$ , and  $2\%$ ,  $d = 20\text{ nm}$ )



in Table 2.5. The spreading exponent,  $\alpha$ , can be used to determine the energy dissipation mechanism. If the dynamic wetting is dominated only by the energy dissipation occurred in the vicinity of contact line, referred to as local dissipation, the molecular kinetic theory (MKT) predicts  $\alpha = 1/7$  [31]. On the contrary, the hydrodynamics model [28–30] assumed that the viscous dissipation in the bulk droplet dominates the dynamic wetting, which predicts  $\alpha = 1/8$  in the gravitational spreading regime and  $\alpha = 1/10$  in the capillary spreading regime.

The fitted spreading exponents,  $\alpha$ , are close to  $1/10$  ( $\Delta = 11\%$  for  $\varphi = 0\%$ ,  $\Delta = 4\%$  for  $\varphi = 0.5\%$ ,  $\Delta = 6\%$  for  $\varphi = 1\%$ , and  $\Delta = 0\%$  for  $\varphi = 0\%$ ), which meets the prediction of the classical hydrodynamics model derived from the bulk viscous dissipation approach for Newtonian flows. Therefore, the bulk dissipation dominates the dynamic wetting of SiO<sub>2</sub>/PDMS500 nanofluids. It should be noted that the super-spreading of nanofluids is controlled by the local energy dissipation, because the super-spreading comes from the structural disjoining pressure due to the

**Table 2.5** Spreading laws of SiO<sub>2</sub>-PDMS500 with various loadings

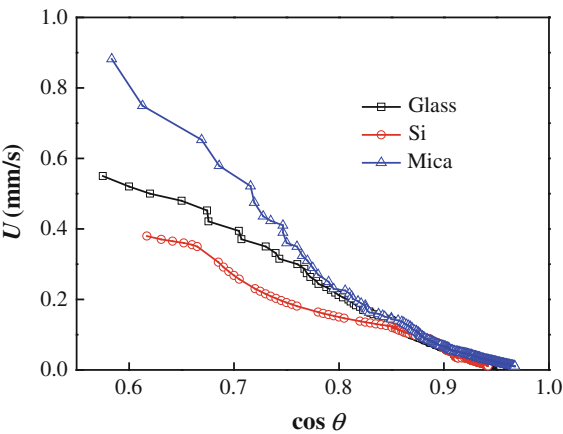
$\varphi$ (%)	$A$	$\alpha$	$R^2$
0	1.366	0.111	0.999
0.5	1.329	0.104	0.999
1	1.277	0.106	0.999
2	1.273	0.100	0.998

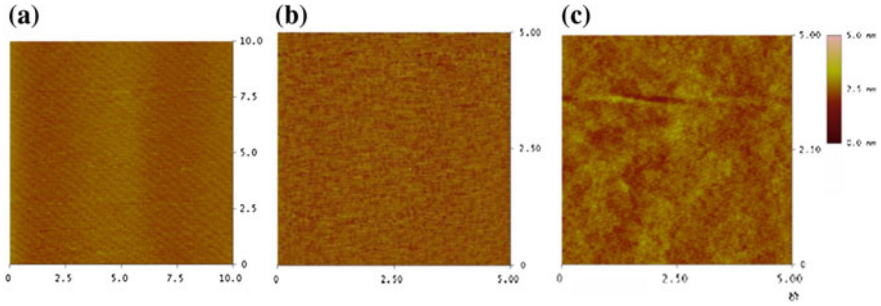
nanoparticle self-assembly near the contact line region. Thus, the bulk dissipation mechanism for dynamic wetting of dilute nanofluids indicates that the nanoparticles do have no enough time to diffuse to the contact line region during the dynamic wetting so that the self-assembly of nanoparticles cannot take place in the present dilute nanofluids. According to the hydrodynamics model, the spreading exponents of about 1/10 also indicate that the capillary force is the only driving force, while the viscous force is the only resistance force. Thus, the role of adding nanoparticles in dilute nanofluids is to change the viscosity and surface tension of nanofluids, and then, these two physical properties affect the dynamic wetting.

2.3.4.2 Nanoparticle Behaviors During Dilute Nanofluid Dynamic Wetting

Figure 2.13 shows the dynamic wetting of SiO<sub>2</sub>/PDMS500 nanofluids ( $d = 20$  nm,  $\varphi = 1$  %) on glass, silicon, and mica slides. The three substrates are chemically and physically homogeneous. The AFM scanning results show that all three surfaces have nanoscale roughness (the root-mean-square roughness is 0.231 nm for glass slide surface, 0.125 nm for the silicon, and 0.137 nm for the mica), as shown in Fig. 2.14. Therefore, the substrates are smooth and ideal surfaces for dynamic wetting [41], so that the dynamic wetting is only affected by the solid surface energy of these three substrates.

**Fig. 2.13** Contact line velocity versus the contact angle for three substrates





**Fig. 2.14** Surface roughness scanning of three substrates using AFM: **a** glass slide; **b** silicon wafer; **c** mica slide

According to MKT [31], the ratio of the contact line velocity to the cosine of contact angle is proportional to the ratio of the liquid–vapor surface tension and the solid–liquid friction coefficient,

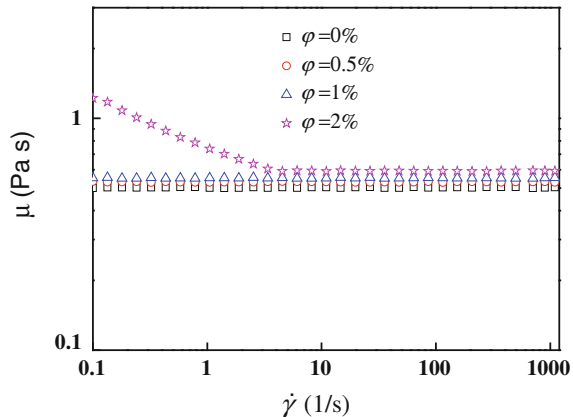
$$U / \cos \theta_D \sim \sigma_{LV} / \zeta, \quad (2.3)$$

where  $\zeta$  is the solid–liquid “friction” coefficient in the MKT model, characterizing the intermolecular interactions between the solid substrate and liquid phase. The  $U - \cos \theta_D$  curves for the three substrates (Fig. 2.10) are linear over most of the droplet spreading time. The ratios of  $\sigma_{LV} / \zeta$  can be obtained from the slopes of the  $U - \cos \theta_D$  curves. With  $\sigma_{LV} = 20.91 \text{ mN m}^{-1}$  for  $\text{SiO}_2/\text{PDMS500}$  nanofluids,  $\zeta$  is  $14.95 \text{ Pa s}$  for the glass slides,  $\zeta = 19.13 \text{ Pa s}$  for the silicon wafer slides, and  $\zeta = 9.03 \text{ Pa s}$  for the mica slides. The “friction” coefficient  $\zeta$  is used to demonstrate that there are no nanoparticles deposited in the vicinity of contact line region during the dynamic wetting. If the self-assembly of nanoparticles occurs in the vicinity of contact line region, the contact line will move on the “ $\text{SiO}_2$  solid surfaces,” no matter what the substrate is; thus, the value of  $\zeta$  for glass, silicon, and mica slides should equal with each other. The different  $\zeta$  indicates that the self-assembly of nanoparticles does not occurs. The results provide an indirect evidence to confirm that the dilute nanofluid dynamic wetting is dominated by the bulk dissipation.

### 2.3.4.3 Newtonian Dynamic Wetting Behaviors of Dilute Nanofluids

It is restated that the  $1/10$  spreading exponent is derived from the hydrodynamics model for the Newtonian dynamic wetting. Thus, the dynamic wetting of dilute nanofluids behaves like that of Newtonian fluids, which is further confirmed by measuring the rheological properties of nanofluids with four nanoparticle loadings ( $\text{PDMS500}$ ,  $\text{SiO}_2$  with  $\varphi = 0, 0.5, 1$ , and  $2 \%$ ,  $d = 20 \text{ nm}$ ), as shown in Fig. 2.15. There is still a debate about whether nanofluids exhibit Newtonian or non-Newtonian behavior [42–48]. Chen et al. [49] and Yu et al. [50] stated that the

**Fig. 2.15** Relation of dynamic viscosity versus shear rate for nanofluids with four nanoparticle loadings ( $\text{SiO}_2$ , PDMS500,  $\phi = 0, 0.5, 1$ , and  $2\%$ ,  $d = 20\text{ nm}$ )



Newtonian or non-Newtonian rheology of nanofluids depends strongly on the nanoparticle volume fraction. The volume-fraction-dependent rheology of nanofluids was explained on the molecular level by considering the effects of the nanoparticle motion and aggregation [40]. In Wang et al.'s work [13, 14], the mass fraction of silica nanoparticles in PPG was 7.5 and 10 %, far higher than the present loadings, which leads to the shear-thickening rheology and hence to the shear-thickening dynamic wetting behavior. However, for the present dilute nanofluids, the nanoparticles distribute uniformly in the bulk liquid. This homogeneous nanoparticle distribution reduces the nanoparticle aggregation in the bulk liquid, leading to the Newtonian-like dynamic wetting behavior.

## 2.4 Conclusions

The variations of wetting radius and contact angle with time were measured using the droplet spreading method to study the dynamic wetting behaviors of dilute nanofluids. Various effects, such as the nanoparticle material, loading, and diameter, the base fluid, and the substrate, were considered in this study. The main conclusions are as follows.

1. The nanoparticles inhibit rather than facilitate the dynamic wetting of dilute nanofluids. Both the contact line velocity and the spreading area decrease with increasing loading. The individual parameter analysis shows that the deterioration in dynamic wetting for dilute nanofluids can be attributed to the increase in either surface tension or viscosity due to adding nanoparticles into the base fluid.
2. The spreading exponent fitted from the nanofluid dynamic wetting data is found to be very close to 0.1, which meets the prediction of the classical hydrodynamics model derived from bulk viscous dissipation approach for Newtonian

flows. This is because the nanoparticles in dilute nanofluids are uniformly distributed in the bulk liquid. The homogeneous nanoparticle distribution reduces the nanoparticle aggregation in the bulk liquid and the self-assembly in the contact line region, leading to a Newtonian-like dynamic wetting behavior.

3. It is interesting that once the effects of the surfaces tension and viscosity are both eliminated using the non-dimensional analysis, the wetting radius versus spreading time ( $R-t$ ) curves for all the nanofluid droplets overlap with each other. This result and the Newtonian-like behavior demonstrate that the dynamic wetting of dilute nanofluids is dominated by the bulk dissipation.

The present results provide a better understanding and direct evidences of the bulk dissipation mechanism for the dilute nanofluid dynamic wetting. The finding of Newtonian-like behavior in dilute nanofluids also provides a guideline for building theoretical models of the dynamic wetting of dilute nanofluids.

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Dynamic Wetting by Nanofluids

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2016, XIII, 112 p. 75 illus., 2 illus. in color., Hardcover

ISBN: 978-3-662-48763-1