Applied Surface Science 256 (2010) 7260–7264

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Wetting of liquid droplets on two parallel filaments

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ARTICLE INFO

Article history:
Received 18 February 2010
Received in revised form 14 May 2010
Accepted 14 May 2010

Keywords:
surface wetting
wetting length
droplets
filaments
contact angle

ABSTRACT

Droplet wetting on two parallel filaments may assume a barrel-shaped morphology or a liquid bridge depending upon the filament diameter and spacing, droplet volume, and contact angle. This paper is aimed to examine the dependency of droplet wetting length upon the above parameters. In the process, morphology of either a barrel-shaped droplet or a liquid bridge sitting on two parallel filaments is determined numerically by using surface finite element method (SFEM). Variation of wetting length with contact angle is examined at varying droplet volume, filament spacing, and droplet morphology. It is found that the droplet wetting length increases with decreasing filament spacing ratio as well as contact angle while it also increases with the growth of droplet volume. The dependency of wetting length upon contact angle behaves sensitive to filament spacing in the case of stable liquid bridges, while it exhibits nearly constant sensitivity to the contact angle in the case of barrel-shaped droplets. The quantitative relations yielded in this study can be considered as characteristic curves applicable for a variety of droplet-on-filament systems, particularly useful to wetting property characterization of filaments, micro liquid delivery, biological cell manipulation, etc.

1. Introduction

Droplet-on-filament is a typical microfluidic system that is commonly observed in life experiences and engineering practices such as wetting of a spider web by morning dew and dyeing and cleaning of fabrics and textiles. Droplet-on-filament system has been extensively employed to characterize the contact angle of liquids. For a typical droplet-on-filament system in the form of a droplet sitting on a monofilament or between two filaments, the droplet morphology and wetting length on the filament(s) are implicit functions with respect to the filament geometries and contact angles. In the last three decades, substantial effort has been dedicated to understanding the wetting and spreading behavior of droplets on filaments [1–8]. Among these, Carroll [9] was the pioneer to first obtain the mathematical expression of a barrel-shaped droplet wetting symmetrically on a filament in term of combination of Legendre's elliptical function of the first and second kinds. Carroll's solution and interpretation has been used as one of the standard methods to extract the contact angle of liquids wetting on filaments [6]. Based on Carrol's formulation, several follow-up studies have been devoted to enhancing the accuracy of determination of contact angles based on experimental measurements of droplet-on-filament systems [10–12]. As a matter of fact, two possible droplet morphologies can be assumed when a droplet wets on a filament, i.e. the barrel-shaped morphology corresponding to the case of a droplet with a large volume and the clamshell-shaped morphology relating that of a low droplet volume. The actual stable droplet morphology detectable in experiments is the one relevant to the lower surface energy which depends upon the characteristic parameters of the system, i.e. filament diameter, droplet volume, and surface tension. Recently, McHale et al. [13] and McHale and Newton [14] have identified the critical condition of morphology transition between a barrel-shaped and a clamshell-shaped morphology in term of the critical droplet volume at a given filament diameter and contact angle. The determination was based on an efficient surface finite element method (SFEM), i.e. the Surface Evolver package developed by Brakke [15]. In their augments [13,14], a droplet sitting on a given filament will keep the clamshell-shaped morphology till the droplet volume exceeds a threshold value, at which morphology transition happens. As a result, the critical condition of morphology transition of droplets can be obtained in term of a characteristic wetting curve in term of the critical droplet volume vs. the contact angle. Besides, the wetting length of a barrel-shaped droplet can be calculated analytically according to Carrol's pioneering work [9].

Nevertheless, the above theories of droplet-on-filaments excluded the interaction of neighboring filaments. Thus, rich information regarding liquid delivery and manipulation is untouched though they are extremely important in modern science and technological applications. It is expected that study of droplet wetting

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doi:10.1016/j.apsusc.2010.05.061

and spreading on multiple filaments, yarns, fiber networks and fiber assemblies, etc. would provide substantial knowledge and novel experimental techniques useful to broad applications. Among these, the simplest case is a droplet wetting and spreading on two parallel filaments. By using an asymptotic scheme, Princen [16–18] first considered the capillary rises in two and multiple vertical micro cylinders (filaments) and the wetting lengths of droplets sitting on two and multiple horizontal cylinders in term of liquid bridges [18]. In Princen's formulation, two implicit assumptions were adopted such that no morphology transition had happened during the process of liquid addition and the droplet volume was large; however this is not always true due to the existence of morphology transition [19]. Furthermore, Keis et al. [20] recently explored the possibility of using parallel filament rails as microfluidic channel to deliver micro and nanoliter liquids. In this case, a kinetic process has been utilized for the scaling analysis and it was concluded that the liquid spreading on the filaments largely followed the Lucas-Washburn spreading law [21,22], i.e. the meniscus displacement is proportional to the complete wicking time (i.e. the time interval from the start of droplet spreading to its disappearance) for a given filament spacing. Clearly, this methodology can also be applied to liquid spreading on multiple fibers and fiber yarns (e.g. wicking).

To study the morphology stability of droplets on multiple filaments, by using a similar approach by McHale [13] and McHale and Newton [14], Wu et al. [19] recently identified the critical condition of morphology transition of a droplet wetting on two parallel filaments of identical diameter and surface wetting properties. In such droplet-on-filament systems, two symmetrical morphologies can be potentially assumed depending upon the droplet volume, i.e. a barrel-shaped droplet which completely enwraps the two filaments and a liquid bridge which partially wets the filament surfaces. Scaling analysis shows that the total surface energy functional of a droplet-on-filament system made of a droplet wetting on two identical parallel filaments can be expressed as

$$\Pi/[(4\pi r^2)\gamma_{LV}] = F[V/(4/3\pi r^3), D/r, \theta], \tag{1}$$

where Π (J) is the total surface energy of the system, γ_{LV} (N/m) the surface tension of the liquid droplet (liquid-vapor interfacial tension), D (m) the filament spacing (i.e. the distance between two filament surfaces), r (m) the radius of the cylindrical filaments, θ the contact angle between the droplet and the filament, and F is a dimensionless function with respect to the dimensionless droplet volume $V/(4/3\pi r^3)$, filament spacing D/r, and contact angle θ. Herein, the reference volume $4/3\pi r^3$ and reference length r have been considered, and gravity and other forces are ignored due to the small characteristic dimension of the system compared to the capillary length of the liquid (See Section 2). A stable droplet morphology based on minimization of (1) corresponds to the global stable state of the system. Morphology transition may happen between a barrel-shaped droplet and a liquid bridge when the two morphologies correspond to the same surface energy at a specific droplet volume. This critical condition can be expressed in term of a family of wetting characteristic curves (*W*-curves) of the critical droplet volume against the filament spacing at varying contact angle [19]. It needs to mention that the above global stability criteria [13,14,19] are different from those of local stability (metastability) based on local energy minimization. The former are corresponding to the global minimum potential energy of droplet-on-filament system while the latter are related to local minimum potential energy (local stationary point of potential energy) of the system. Moreover, when a droplet bridge forms between misaligned filaments, capillary torque is triggered due to breaking of symmetry of the droplet bridge. In this case, the capillary torque can be determined numerically using the Surface Evolver [15], in which a simple numerical differentiation of the surface potential energy with respect to the filament orientation angle can be employed [20] while Virozub et al. [24] utilized surface integration of the capillary force over the position vector of droplet surface points. Since thin filaments are flexible, capillary force due to droplet wetting may further yield filament collapse and contact [25,26] and even fusion which may eventually influence the mechanical behavior of fiber networks [27]. In addition, when a droplet of nano size is wetting on a micro or nanofiber, the recent clamshell model of nano droplet proposed by Berim and Ruckenstein [28] can be considered to explore the effect of interfacial potential between droplet and fiber surface on the droplet morphology. Moreover, hydroelastic analysis of filaments and filamentary materials is still open and new research is expected in understanding of liquids wetting and spreading on flexible soft filaments [29].

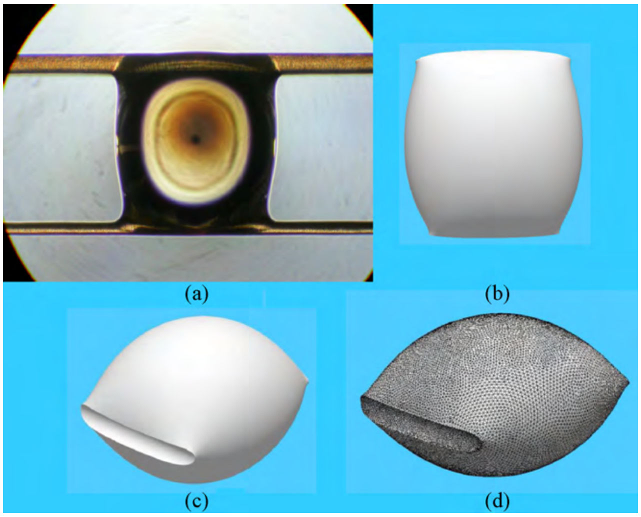

Fig. 1. Wetting of a droplet on two parallel human hair fibers. (*a*) Experimental observation (aerial view) [Fiber spacing: 750 μm, droplet volume: 0.16 mm^3; fiber diameters: 80 μm (upper) vs. 70 μm (below); and contact angles: ~75° vs. ~100° (estimated), experiments were conducted at Ashland Inc., OH]; (*b*) aerial view of the simulated droplet; (*c*) isometric view of simulated droplet; and (*d*) meshes used in the simulation (The actual final meshes used in the simulation were much more denser, filaments in the simulated droplets were not plotted, and the simulation was based on the Surface Evolver) [15].

In practice, our recent experimental effort has been made to apply the droplet-on-filament system to differentiate the wetting properties of human hair fibers for the purpose of haircaring products development. During the process, wetting length of droplets on two parallel hair fibers was considered as a measure to differentiate the wetting properties, and relevant SFEM simulation was performed to validate the experimental observation as shown in Fig. 1. As an extension of our recent investigations [19], this work aims to explore detailed dependency of droplet wetting length upon two parallel filaments in the morphology of either a barrel shape or a liquid bridge. By means of SFEM, detailed numerical simulations were performed to examine the effect of filament spacing, droplet volume, and contact angle. Discussions and potential applications of the results will be made, and concluding remarks of the work will be addressed in the end of the paper.

2. Problem formulation and SFEM simulations

Consider a droplet-on-filament system made of a droplet wetting symmetrically on a pair of parallel filaments of identical diameter and surface properties. Hereafter, we assume that the characteristic dimension of the system (e.g. filament diameter, spacing, or droplet diameter) is less than the capillary length l of

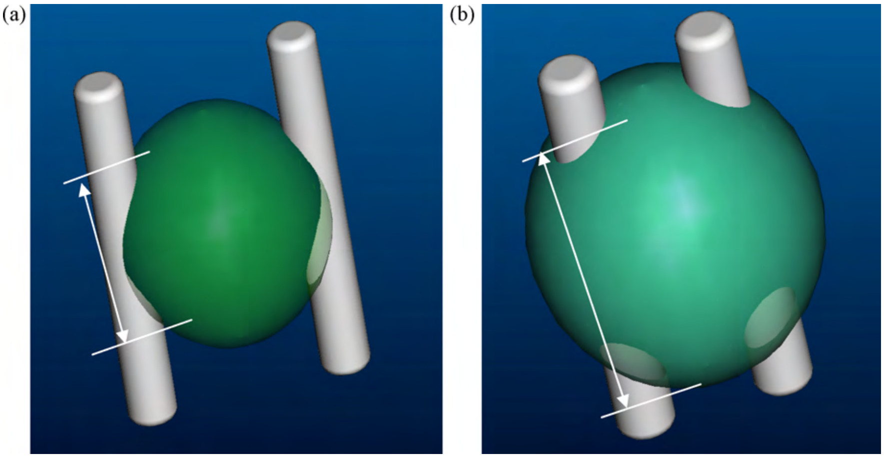

Fig. 2. Illustrations of wetting lengths of (*a*) a droplet bridge and (*b*) a barrel-shaped droplet wetting on two parallel filaments (Pro/Engineer ™ software package was used for the 3D sketching).

the droplet:

$$l = \sqrt{\frac{\gamma_{LV}}{\rho g}}, \qquad (2)$$

where ρ is the mass density of the liquid (ρ=1 g/cm^3 for water), and g is the gravity acceleration (=9.81 m/s^2). For instance, the capillary length of water with the surface tension of 72.8 dyne/cm at 20°C is $l \approx 2.724$ mm, and the characteristic dimensions of the typical droplet-on-filament systems under consideration are below hundreds of microns. Thus, the effect of gravity can be safely ignored. For such a system as illustrated in Fig. 2, two droplet morphologies (e.g. barrel-shaped droplet or liquid bridge) can be possibly assumed depending upon the filament diameter, spacing, droplet volume, and contact angle. The critical condition of morphology transition of a droplet wetting on two parallel filaments can be expressed in term of a family of wetting characteristic curves (*W*-curves) [19]. These *W*-curves can greatly facilitate the study of droplet wetting length in this work since the stable morphology of a droplet wetting on two parallel filaments can be predicted prior to a simulation. Furthermore, wetting length of a droplet on such a droplet-on-filament system (either barrel-shaped or liquid bridge morphology) has a scaling relation:

$$L/r = f[V/(4/3\pi r^3), D/r, \theta], \qquad (3)$$

where L is the wetting length of the droplet, and f is a dimensionless function with respect to $V/(4/3\pi r^3)$, D/r, and θ. However, due to the nonlinear nature and complex geometry of the droplet-on-filament system under consideration, no explicit solution can be expected by directly solving the relevant Young-Laplace equation. Alternatively, with the aid of efficient numerical scheme, an equivalent problem can be reformulated in the view of surface energy variation, i.e. the stable droplet morphology is the one that minimizes the global surface energy of the system. Among others, SFEM (e.g. Surface Evolver) has demonstrated its great flexibility and powerful capacity of solving such types of droplet-on-filament problems as reported recently [19,23,24]. Thus, in this study, SFEM is further implemented in determining the stable droplet morphology of the system. Droplet wetting length is extracted graphically using the droplet morphology as illustrated in Fig. 3. To enhance the accuracy and efficiency of the simulation, 1/8-models (see Figs. 4 and 5) have been adopted in the entire investigation as considered recently by the authors [19].

Furthermore, contact angle is an important microfluidic parameter which plays crucial role in a variety of droplet-on-filament systems including resin permeating in fiber composite processing, fabric dyeing and cleaning, chemical treatment of human hair fibers, etc. Thus, the present study investigated the wetting lengths on two parallel filaments wetted by hydrophilic, neutral, and hydrophobic droplets, respectively. During the numerical process, five contact angles (θ=30°, 60°, 90°, 120° and 150°), three dimensionless spacings (D/r = 1, 2 and 3), and four dimensionless droplet volumes [$V/(4/3\pi r^3)$ = 15 and 30 for droplet bridges

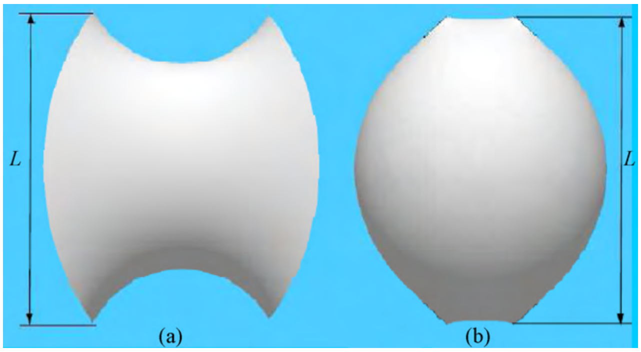

Fig. 3. Definitions of wetting length of (*a*) a droplet bridge and (*b*) a barrel-shaped droplet wetting between two parallel filaments (filaments were not plotted).

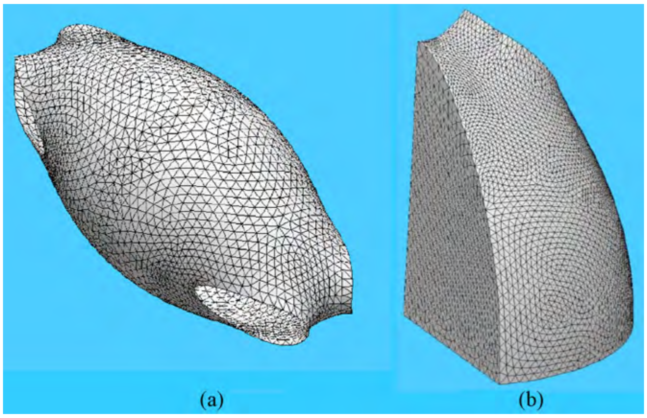

Fig. 4. Meshes used for the simulation of a barrel-shaped droplet wetting on two parallel filaments of identical diameter and surface properties: (*a*) Full model and (*b*) 1/8-model (Filaments were not plotted, the simulation was based on the Surface Evolver [15] with filament radius: r = 1; filament spacing: D = 2; droplet volume V = 400; and contact angle: θ=30°, the actual final meshes are much denser and not plotted herein) [19].

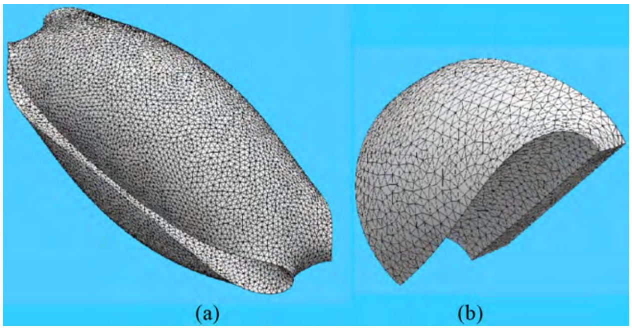

Fig. 5. Meshes used for the simulation of a droplet-bridge wetting on two parallel filaments of identical diameter and surface properties: (*a*) Full model and (*b*) 1/8-model [Filaments were not plotted, the simulation was based on the Surface Evolver [15] with filament radius: $r = 1$; filament spacing: $D = 2$; droplet volume $V = 400$; and contact angle: $\theta = 30^o$, the actual final fine meshes are much denser and not plotted herein] [19].

and $V/(4/3\pi r^3) = 250$ and 400 for barrel-shaped droplets] were used. Selection of the droplet volume guaranteed that the droplets assumed the stable morphologies as expected according to the *W*-curves [19]. For a particular case of simulation, the numerical process was terminated when the relative numerical errors of surface energies of two sequential iterations were less than 1%.

3. Results and Discussion

Dependency of wetting length (*L*/*r*) of droplets sitting on two parallel filaments has been examined through detailed numerical simulations using the Surface Evolver. Numerical results are plotted in Figs. 6-9. For relatively low droplet volumes (i.e. $V/(4/3\pi r^3) = 15$ and 30), stable liquid bridges are formed on the droplet-on-filament systems with the parameters given in Section 2. Such stable morphologies are expected according to the *W*-curves [19]. Variations of the dimensionless wetting length with the contact angle at three filament spacing ratios ($D/r = 1$, 2, and 3) are shown in Figs. 6 and 7. For given droplet volumes, Figs. 6 and 7 show that the wetting lengths decrease with increasing either contact angle or filament spacing ratio. This follows the common sense that more quantity of liquid can wet larger surface area. Besides, at large spacing ratio (e.g. $D/r = 3$), wetting length is largely insensitive to contact angle. In contrast, at low spacing ratio (e.g. $D/r = 1$), wetting length is highly sensitive to contact angle. Thus, such effect is expected more pronounced with further decreasing spacing ratio as more obvious

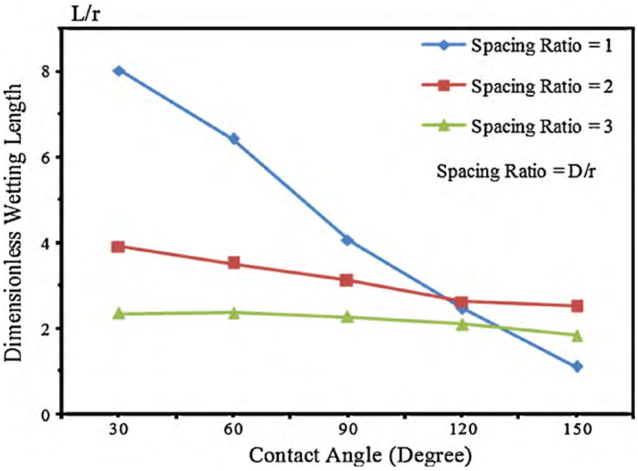

Fig. 6. Variation of the wetting length vs. the contact angle for liquid-bridges wetting between two parallel filaments [dimensionless volume: $V/(4/3\pi r^3) = 15$].

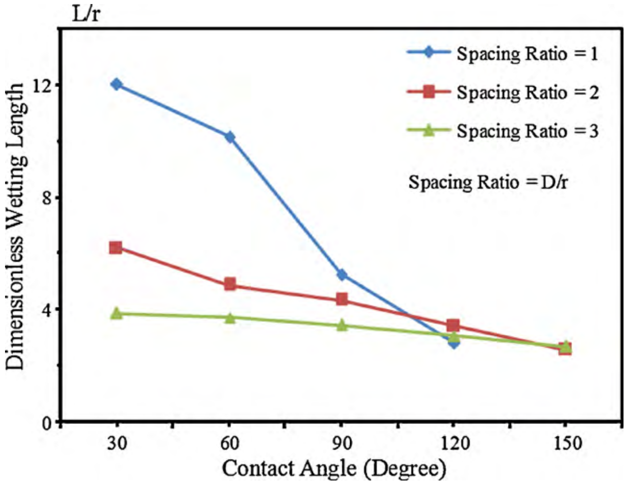

Fig. 7. Variation of the wetting length with the contact angle for liquid-bridges wetting between two parallel filaments [dimensionless volume: $V/(4/3\pi r^3) = 30$].

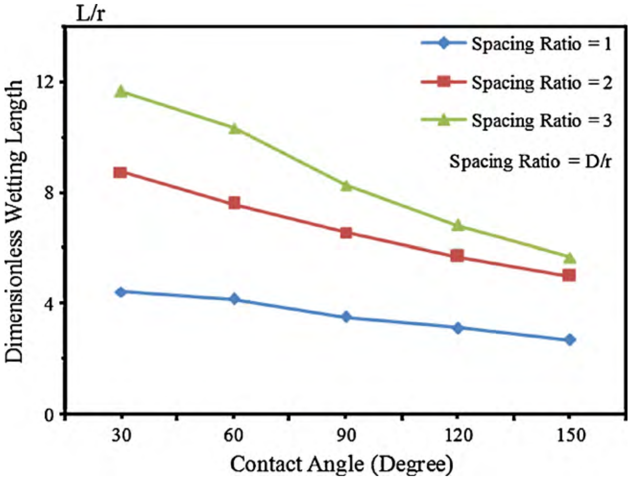

Fig. 8. Variation of the wetting length vs. the contact angle for barrel-shaped droplets wetting on two parallel filaments [dimensionless volume: $V/(4/3\pi r^3) = 250$].

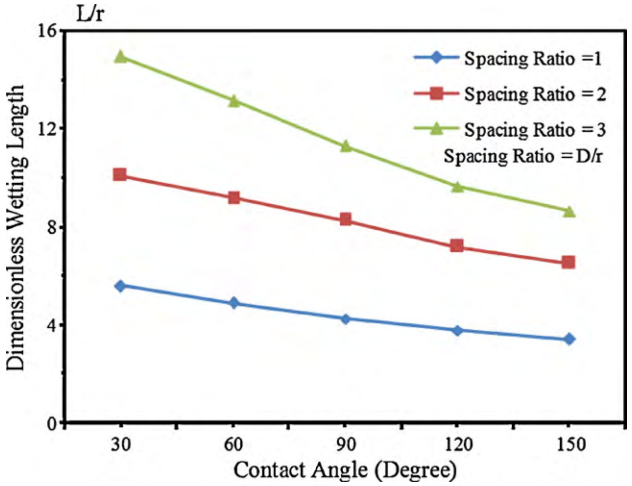

Fig. 9. Variation of the wetting length vs. the contact angle for barrel-shaped droplets wetting on two parallel filaments [dimensionless volume: $V/(4/3\pi r^3) = 400$].

capillary effect exhibits due to change of sign of the principal radius of curvature of the droplet surface at wetting fronts. However, very small spacing ratio will lead to difficulties in numerical simulation since the wetting length becomes extremely large. As a result, numerical simulations have indicated the potential and limitation of surface treatment (contact angle) to modulate the liquid delivery and manipulation based on droplet-on-filament systems.

Furthermore, for droplets with relatively large quantity of volumes [e.g. $V/(4/3\pi r^3) = 250$ and 400], stable barrel-shaped droplets were formed in the parallel filaments based on the *W*-curves [19]. In this case, numerical results show that the diagrams of dimensionless wetting length vs. contact angle largely keep a nearly linear relationship at three filament spacing ratios (i.e. $D/r = 1$, 2, and 3) under consideration as plotted in Figs. 8 and 9. Different from the cases of liquid bridge, wetting lengths of barrel-shaped droplets keep almost the similar sensitivity to the contact angle at three filament spacing ratios as examined in this study though it also has the trivial increase with growing droplet volume. Therefore, in this case, surface treatment would be a favorable method to tailor the wetting length of the droplet.

4. Concluding Remarks

Detailed numerical simulations have been demonstrated in examining the dependency of wetting length of droplet on two parallel filaments upon a variety of system parameters (e.g. filament spacing ratio, droplet volume, and contact angle). In the study, determination of stable morphology of a droplet wetting on filaments is crucial in view of both experimental and theoretical studies because a predictable stable morphology represents detectable droplets in reality and it can also significantly simplify the simulation process. Numerical simulations have indicated that the sensitivity of droplet wetting length to contact angle highly depends upon the droplet morphology assumed on the filaments.

The quantitative relations gained in this study are applicable to determination of the surface wetting properties of various liquids on filaments. These results can be utilized to design filament systems for the purpose of manipulation and delivery of a small volume of liquid and even biological cells in high resolution. Moreover, with development of recent low-cost techniques for ultrathin fiber fabrication (e.g. electrospinning), nanofilamentary materials have been finding rapidly growing applications, especially in biological systems and nanocomposites. It can be expected that the present research would shine the lights into the study of wetting and spreading properties of nanofilamentary materials.

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