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Effects of surface wettability on gecko adhesion underwater

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ABSTRACT

Recent experiments have shown that gecko adhesion underwater depends significantly on surface wettability. Theoretical models of a gecko seta adhering on different substrates are firstly established in order to disclose such an adhesion mechanism. The results show that the capillary force induced by nano-bubbles between gecko seta and the substrate is the mainly influencing factor. The capillary force exhibits an attractive feature between gecko setae and hydrophobic surfaces underwater. However, it is extremely weak or even repulsive on hydrophilic surfaces underwater. A self-similarly splitting model is further considered to simulate multiple gecko setae on substrates underwater. It is interesting to find that the total capillary force depends significantly on the number of nano-bubble bridges and wettability of substrates. The total force is attractive and increases monotonically with the increase of the splitting number on hydrophibic substrates underwater. However, it decreases drastically or even becomes repulsive on hydrophilic substrates underwater. The present result can not only give a reasonable explanation on the existing experimental observations but also be helpful for the design of novel biomimetic adhesives.

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1. Introduction

Geckos' amazing adhesion ability had stirred significantly scientific research interests, which could be traced back to the 4th century B.C. [1]. However, until recent decades, extraordinary progresses have been made in understanding how geckos could climb on and detach from almost any surface at will [2–8]. Micro-structures of gecko adhesion system were observed and the fundamental adhesion principle was disclosed experimentally [2,8]. It has been well known that one gecko toe has a lot of lamella structures consisting of thousands of setae and each seta further branches into hundreds of spatulae with nano-scales (5–10 nm in thickness, 200 nm in length and width), typically belonging to a hierarchical structure. Such an adhesion system ensures gecko to obtain strong adhesive force on almost any surface, whether hydrophilic or hydrophobic, rough or smooth [1,2,8].

Experimental and theoretical studies on gecko adhesion mechanisms have been carried out extensively during the past decades, most of which mainly focus on the van der Waals adhesion mechanism on dry solid surfaces [5,8–11]. However, there are more than 1400 species of geckos in the world and different species possess different natural habitats and living conditions [12]. Geckos in

http://dx.doi.org/10.1016/j.colsurfb.2014.07.047 0927-7765/© 2014 Elsevier B.V. All rights reserved. tropical rainforests may usually encounter or live on wet surfaces. For example, arboreal geckos like to inhabit on hydrophobic plant surfaces more than other substrates in wet environments [13]. But the van der Waals force is known to decrease drastically in water due to the small Hamaker constant. How do such geckos achieve strong adhesion in wet environments?

Only few literatures have studied the wet adhesion mechanism of geckos so far [14–20]. Huber et al. [14], Sun et al. [16] and Pesika et al. [19] have experimentally proved that capillary force also plays a significant role in gecko adhesion besides the van der Waals force and the adhesive force increases with the increase of relative humidity. However, geckos cannot adhere on hydrophilic glass surfaces once sprayed with water [16,17]. Theoretical analysis of why the relative humidity and sprayed water yield two different effects on gecko adhesion has been investigated in one of our previous works [15]. The disjoining pressure induced by the interlayer water film was found to enhance gecko adhesion. With the increase of relative humidity, water droplets will form and be wrapped by the thin-film-like spatula [21], leading to a drastic decrease of the adhesive force [15].

Recently, systematic experiments of gecko adhesion on different substrates under different conditions have been carried out by Stark et al. [17,18]. It is found that the dry adhesion strength of geckos is extremely strong on both hydrophilic and hydrophobic substrates. When the substrates are submerged in water, gecko adhesion is hardly affected by the aqueous environment, remaining

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Fig. 1. The interference fringes (left) measured by spectrometer and the deduced interface configuration (right) for two interacting mica surfaces coated with LB (Langmuir–Blodgett) films of hydrocarbon surfactant (a) and fluorocarbon surfactant (b), where the discontinuity in the fringes (left) indicates the vapor-water interface and gaseous meniscus bridging the two contacting surfaces (right). *Source:* Taken from H.K. Christenson and P.M. Claesson, Science, 239 (1988), 380–392 [30]

strong adhesion on hydrophobic substrate surfaces, but drastically decreases on hydrophilic ones. Furthermore, it is well known that geckos cannot adhere well on dry polytetrafluoroethylene (PTFE) surfaces due to the extremely small surface energy, which is not true anymore underwater. The adhesive force on a PTFE surface underwater is vastly improved in contrast to the dry case [18,22]. All the phenomena suggest that surface wettability may play a significant role in gecko adhesion underwater.

In fact, the interaction between two hydrophobic surfaces in aqueous environments fascinated many researchers in the last decades due to the strong and inconceivably long-ranged (20–300 nm) attraction [23]. Many possible mechanisms have been proposed, including entropic effects, electrostatic effects, correlated charge fluctuation and nanoscale bubble bridging [24,25]. Most of experiments have shown that cavitations or nano-bubbles can spontaneously form on hydrophobic surfaces as soon as they are brought into water [26-32]. A surprising finding is that nanobubbles on surfaces are closely packed with a coverage even close to 100%, depending on the chemistry and roughness of surfaces [26,28]. When one hydrophobic surface approaches the other hydrophobic one underwater, they found a strong long-ranged hydrophobic attraction between the two approaching hydrophobic surfaces, which is verified experimentally that the source of the hydrophobic force is due to the coalescence of nano-bubble bridges between them [26-31] as shown in Fig. 1. Due to the superhydrophobicity of gecko's toes [33,34], it is reasonable to infer that nano-bubbles can form on gecko's foot and contribute to gecko adhesion underwater.

Though many experimental investigations have shown the effects of nano-bubble bridges on the long-ranged adhesive force between two hydrophobic surfaces underwater, theoretical studies on such an adhesion mechanism are still lacking [35,36]. Furthermore, what is the possible mechanism of gecko adhesion on substrates underwater? What are the main factors that influence gecko adhesion on wet surfaces? Both questions are unclear and will be answered theoretically in the present paper.

2. A theoretical model of wet adhesion for geckos

2.1. Geometries of gaseous menisci induced by interfacial nano-bubbles

Nano-bubbles can spontaneously form on solid hydrophobic surfaces underwater [26,28–32] and images measured by AFM



Fig. 2. Schematic of a gecko seta described by a cylindrical fibril with a hemispherical tip in contact with a substrate underwater. A nano-bubble meniscus spontaneously forms at the interface. *R* is the radius of the fibril and *D* the separation; φ is the filling angle and ϕ the angle between the normal direction of the meniscus and *y* axis. θ_1 and θ_2 are contact angles of the fibril and substrate, respectively.

exhibit that the radius of nano-bubbles usually has an order of magnitude 100 nm, which could coalesce to form a larger gaseous bridge between surfaces [28,30,37]. Fig. 2 shows a gecko seta adhering on a solid surface underwater with a nano-bubble meniscus bridging them. Since the capillary interaction feature between a fiber and a flat substrate does not depend significantly on the fiber's tip shape (flat, cylinder, sphere, etc.) [38–40], gecko seta is modeled as a cylindrical fibril with a hemispherical tip in the present paper for simplicity and without loss of generality [3,4,11,20]. R is the radius of the fibril as well as that of the hemispherical tip. D is the distance between the hemispherical tip and the substrate. φ is the filling angle of the nano-bubble on the hemispherical tip. The contact angle of water on the fibril is θ_1 and that on the substrate surface is θ_2 . One should note that the present model with a gaseous meniscus is very similar to the real experimental observations [31,32] and theoretical models with a liquid bridge [20,38,41-44].

The ordinary differential equation describing the profile of the gaseous meniscus can be derived from the Young-Laplace equation as [41–43]

$$\frac{dx}{ds} = \cos\phi,\tag{1a}$$

$$\frac{dy}{ds} = \sin\phi,\tag{1b}$$

$$\kappa = \frac{d\phi}{ds} + \frac{\sin\phi}{x},\tag{1c}$$

where x and y are coordinates of the axisymmetric meniscus. ϕ is an angle between the normal direction of the meniscus and y axis as shown in Fig. 2. s and κ are the arc length and mean curvature of the nano-bubble profile, respectively.

Boundary conditions of the profile function can be written as

$$\begin{cases} x_1 = R\sin\varphi, \quad y_1 = D + R(1 - \cos\varphi), \quad \phi = 180^\circ + \varphi - \theta_1 \\ y_2 = 0, \quad \phi = \theta_2 \end{cases}$$
(2)

Eqs. (1) and (2) form a boundary-value problem. It is easy to obtain the profiles of nano-bubble menisci between the fiber and substrates with the help of numerical calculation, which is shown in Fig. 3 for cases of different contact angles and nano-bubble volumes.

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