Gecko adhesion pad: a smart surface?

Noshir S Pesika[1,7]**, Hongbo Zeng**[2]**, Kai Kristiansen**[3]**, Boxin Zhao**[4]**, Yu Tian**[5]**, Kellar Autumn**[6] **and Jacob Israelachvili**[3]

[1] Chemical and Biomolecular Engineering Department, Tulane University, New Orleans, LA 70118, USA
[2] Chemical and Materials Engineering Department, University of Alberta, Edmonton, AB, T6G 2V4, Canada
[3] Chemical Engineering Department, University of California, Santa Barbara, CA 93117, USA
[4] Chemical Engineering Department and Waterloo Institute of Nanotechnology, University of Waterloo, Ontario, N2L 3G1, Canada
[5] State Key Laboratory of Tribology, Department of Precision Instruments, Tsinghua University, Beijing 100084, People's Republic of China
[6] Department of Biology, Lewis and Clark College, Portland, OR 97219, USA

E-mail: npesika@tulane.edu

Abstract

Recently, it has been shown that humidity can increase the adhesion of the spatula pads that form the outermost (adhesive) surface of the tokay gecko feet by 50% relative to the main adhesion mechanism (i.e. van der Waals adhesive forces), although the mechanism by which the enhancement is realized is still not well understood. A change in the surface hydrophobicity of a gecko setal array is observed when the array, which supports the spatulae, is exposed to a water drop for more than 20 min, suggesting a change in the hydrophilic–lyophilic balance (HLB), and therefore of the conformation of the surface proteins. A surface force apparatus (SFA) was used to quantify these changes, i.e. in the adhesion and friction forces, while shearing the setal array against a silica surface under (i) dry conditions, (ii) 100% humidity and (iii) when fully immersed in water. The adhesion increased in the humid environment but greatly diminished in water. Although the adhesion forces changed significantly, the friction forces remained unaffected, indicating that the friction between these highly textured surfaces is 'load-controlled' rather than 'adhesion-controlled'. These results demonstrate that the gecko adhesive pads have the ability to exploit environmental conditions to maximize their adhesion and stabilize their friction forces. Future designs of synthetic dry adhesives inspired by the gecko can potentially include similar 'smart' surfaces that adapt to their environment.

1. Introduction

The gecko adhesive pad, which consists of several hierarchical structures ranging from the micron to nanometer length scale [1–4], as shown in figure 1, has been studied extensively because of its amazing adhesion and friction properties that allow geckos to climb walls and walk on ceilings. Geckos live mostly in deserts and warm tropical and sub-tropical areas, i.e. in places of low humidity, but they are also commonly found in tropical rain forests. Thus, they are well adapted to *both* extremely dry *and* wet conditions. This adaptability is the main subject of this paper. Autumn *et al* [3] showed that the weak van der Waals forces between the numerous spatula pads ($\sim$10 nm thick by 200 nm wide keratinous pads that form the final hierarchical structures (see figure 1(F)) and different surfaces are responsible for the resulting high adhesion and friction forces. The different levels of hierarchy in the gecko setal arrays result in an effective modulus significantly lower [5–7] than that of the material of which it is composed, i.e. β-keratin, thus allowing the setal array to conform to surfaces of varying roughness. In addition, the way these hierarchical structures are articulated [2, 8, 9], which result in pulling forces acting at small angles from the surface, significantly enhance the adhesion force [2, 10]. Since van der Waals forces are universal, a synthetic dry adhesive inspired by the gecko adhesive system is desirable for applications ranging from

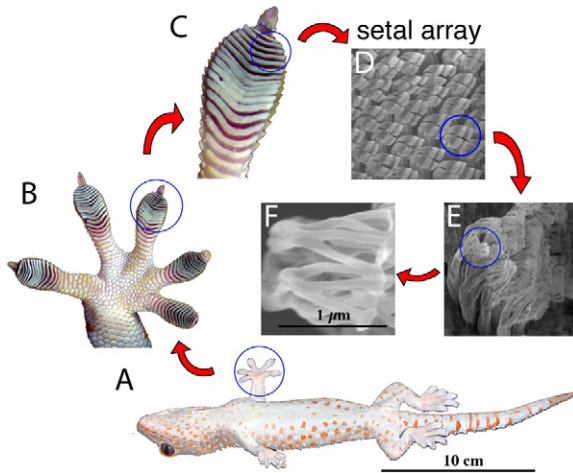[7] Author to whom any correspondence should be addressed.

Figure 1. Hierarchical structures of the tokay gecko. Optical image showing (A) an inverted gecko at rest, (B) a gecko foot and (C) a gecko toe. Scanning electron microscope images of (D) a setal array, (E) the spatula pads and (F) a magnified view of the spatula pads. Reproduced with permission from [10] ©2006 National Academy of Sciences, USA.

(This figure is in colour only in the electronic version)

adhesives on robotic appendages to commercial adhesive tapes. Furthermore, dry adhesives relying on van der Waals forces are expected to work in any environment, including vacuum or in aqueous media.

Several synthetic dry adhesives have been fabricated in recent years [11–18] and the main focus has been on the geometrical design (i.e. dimensions and spacing of the pillars that mimic the setae, shapes of the tips that mimic the spatula pads) of the hierarchical structures and the mechanical properties of the material (for example, Young's modulus, elasticity and yield strength). Fewer synthetic adhesives based on the gecko have incorporated surface chemistry into their design to enhance adhesion. The hybrid design of Lee *et al* [19] uses a thin mussel–mimetic polymer coating over an array of nanostructured pillars and polymer pillars. These structures are capable of reversible adhesion in dry or wet environments.

Recently, it has been shown that gecko adhesion is enhanced when present in a humid environment [20, 21] while the adhesion is drastically reduced (ascertained through observations that geckos fall off surfaces when sprayed with water), although the mechanisms by which the adhesion force changes is still not well understood. The adhesion force F_a between surfaces can be related to the thermodynamic surface energy γ_{sv} by

$$F_a = C(r)\gamma_{sv}, \tag{1}$$

where $C(r)$ depends on the geometry of the contacting surfaces and r is the local radius of curvature [22]. By the Gibbs' adsorption isotherm [23]:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln c}, \tag{2}$$

where Γ is the surface excess, R is the gas constant, T is temperature, c is the species concentration and γ is the surface energy, the adsorption of species (e.g. water molecules) to an

interface leads to a decrease in the surface energy. Therefore, the adhesion force F_a must also decrease. An increase in adhesion would imply a change in the surface chemistry resulting in a change in the surface energy.

Leckband *et al* [24] demonstrated that the hydrophobicity of a lipid-protein monolayer is not an intrinsic property of that surface but depends on the environment. They hypothesized that the surface proteins undergo a conformational change (for example, presenting hydrophilic groups when exposed to high humidity or aqueous media). Here, we present evidence that the keratinous setal arrays of a tokay gecko can also change their hydrophilic–lyophilic balance (HLB), or surface wetting properties, when exposed to water using a similar mechanism described by Leckband *et al* [24]. In a dry environment, geckos rely entirely on van der Waals forces to adhere to surfaces. When present in a humid environment, geckos can enhance their adhesion by exploiting the increased surface energy as a result of conformational changes in the surface proteins of their adhesive pads. In addition, we demonstrate that adhesion and friction forces are still present between a gecko setal array and a silica surface while under water.

2. Experimental details

2.1. Drop contact experiments

The gecko setal array was carefully positioned and glued (Loctite 410; Henkel Loctite Cr., Rocky Hill, CT) on the end of a Pasteur pipette. A small droplet of deionized water ($\sim$2 µl) was created using a syringe and was brought into contact with the gecko setal array as shown schematically in figure 2(A). The exposure time of the water droplet to the setal array was recorded. The experiment was performed on the stage of an inverted optical microscope using a $40\times$ objective and videos were captured using a CCD camera (Pulnix TM-200, Jai Pulnix Inc.) connected to a videocassette recorder. The microscope light was turned off during the drop contact step to minimize the evaporation of the water drop. All experiments were performed under ambient humidity (50%) and temperature (23 °C).

2.2. SFA measurements

A surface force apparatus (SFA 2000) was used to measure the lateral (friction F_f) and normal (adhesion F_a) forces of setal arrays against a silica surface. The gecko setal arrays were from live nonmolting tokay geckos using the methods described by Autumn *et al* [3]. A setal array ($\sim$0.5 mm wide and $\sim$3 mm long) was glued onto the ridge of a cylindrically curved surface ($R = 2$ cm) of a silica disc with cyanoacrylate adhesive (Loctite 410; Henkel Loctite Corp., Rocky Hill, CT) and mounted as the bottom surface supported by a double cantilever spring, which was connected to a bimorph slider. The 'top' surface was a bare optical polished silica disc surface with the same cylindrical curved shape, and was cleaned by exposure to UV–ozone for 3 min prior to experiments. The two curved surfaces were mounted in the SFA chamber in a crossed-cylinder geometry, which corresponds approximately to a sphere of radius R on a flat based on the Derjaguin
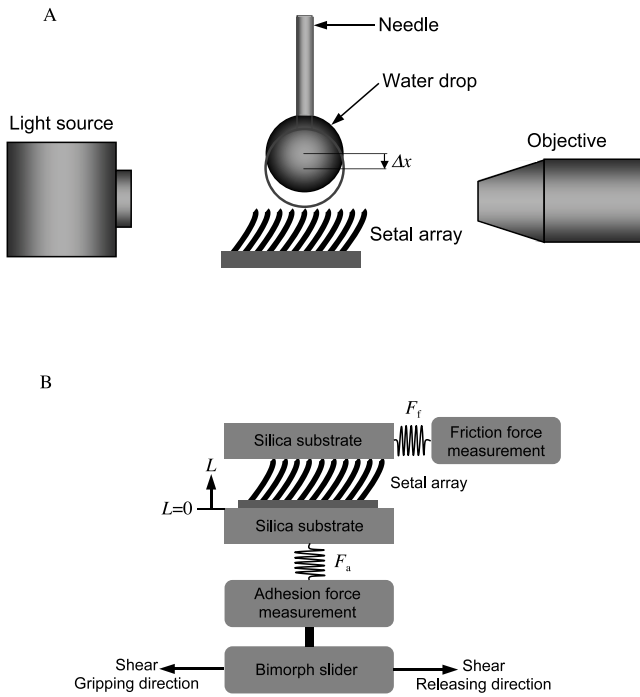
A

B

Figure 2. Schematic illustration of the experimental set-up to (A) visualize the contact between a water drop and the setal array using an inverted microscope with a 40× objective and an attached video camera and (B) measure the adhesion and friction force generated while shearing a silica surface against the setal array in the gripping direction using an SFA with a 'friction device' and a bimorph slider.

approximation. Lateral (or shear) movement of the bottom surface was accomplished with a piezoelectric bimorph slider, and the adhesion and friction forces were measured using a 'friction device' [25]. The experiments were performed at room temperature (23 °C).

The friction F_f and adhesion F_a between the setal arrays and the silica glass surface were studied in three different conditions: (i) dry N_2 atmosphere with a P_2O_5 reservoir; (ii) 100% humidity with a water reservoir in the sealed SFA chamber and (iii) fully immersed in pure Milli-Q water following a similar procedure as Zhao *et al* [26]. The experiments were initiated after the surfaces had been mounted in the sealed SFA chamber with desired environments for at least 1.5 h. During the experiments, the lower surface was brought into contact with the upper surface, and a finite load was applied. The lower surface was driven back and forth laterally at a fixed velocity 10 μm s^{-1}, and the peak-to-peak sliding amplitude was ~110 μm. For each load, the sliding was stopped while shearing in the gripping direction with the bimorph at roughly the same position as the position at initial contact. The surfaces were then separated and the normal adhesion force was measured through the deflection of the spring.

3. Results and discussion

Figure 3(A) shows a series ((i)–(iii)) of optical images of a water drop brought into contact with a setal array followed by the retraction of the water drop. The setal array is initially

superhydrophobic. The adhesion between the water drop and the surface of the setal array is weak as observed from the negligible deformation of the droplet as it is retracted from the setal array. Figure 3(B) shows a series of images from a similar experiment after allowing a water drop to be in contact with the setal array for 20 min. The adhesion between the setal array and the water drop increases as inferred from the neck formation (figure 3(B)-(iii)) when the water drop is retracted from the setal array. The drop continues to deform as it is pulled away until separation between the setal array and the water drop within the neck region. As a result, a thin water film (compare figures 3(B)-i–(B)-iv) is left behind on the setal array covering the area that was exposed to water. Subsequent contacts of water drops to the same area (i.e. the region previously exposed to water) lead to the 'wicking' of water into the array (compare figures 3(B)-iv to (B)-v and (B)-vi).

Our observation is consistent with a Cassie to Wenzel transition [27]. Although the majority of studies on superhydrophobic surfaces have focused on the geometrical factors that contribute to either the Cassie or Wenzel state, fewer studies have explored the potential chemical contribution [28]. The setal array, which consists of an array of β-keratin pillars, is initially superhydrophobic, with a contact angle of ~160° [29]. For comparison, the contact angle of a water drop on a flat surface of β-keratin (the gecko spectacle; a thin layer of flat skin covering the eye of the gecko) is ~93° [29]. In the presence of water, we hypothesize that a change the hydrophilic–lyophilic balance (HLB) of the surface leads to the overturning of surface proteins, thus making the setal array less hydrophobic or increasing its surface energy (a contact angle smaller than 90°). This subtle change in the contact angle of surface proteins results in the transition from a Cassie to a Wenzel state, in which water penetrates the gaps between the setal stalks. The modified (less hydrophobic) region of the setal array remains in the higher energy state for a prolonged time (>48 h) when stored under ambient temperature and humidity, suggesting either that the transition is irreversible or the kinetics of the surface proteins overturning to their original configuration occurs on a slow timescale. The details of the overturning mechanism of the surface proteins are still being investigated.

Since the setal arrays adhere to surfaces through van der Waals interactions, it is expected that both the adhesion F_a and friction F_f forces of the setal array against another surface are still present underwater. Figures 4(A) and (B) show the adhesion and friction forces measured by the SFA, generated during the shearing of the setal array against a silica surface in the gripping direction (i.e. the shear direction which geckos use to attach to a surface) under varying conditions; (i) dry, (ii) 100% humidity and (iii) fully immersed in water. Under all three conditions, the adhesion force between the setal array and the silica surface increases as the load L is increased. The increase in the adhesion force as a function of the load is due to an increase in the number of contacts between the spatula pads and the silica surface [26]. Under dry conditions (circles in figure 4(A)), the setal array is superhydrophobic and only van der Waals interactions are present. When exposed to a 100% humidity environment (squares in figure 4(B)) for a sufficient
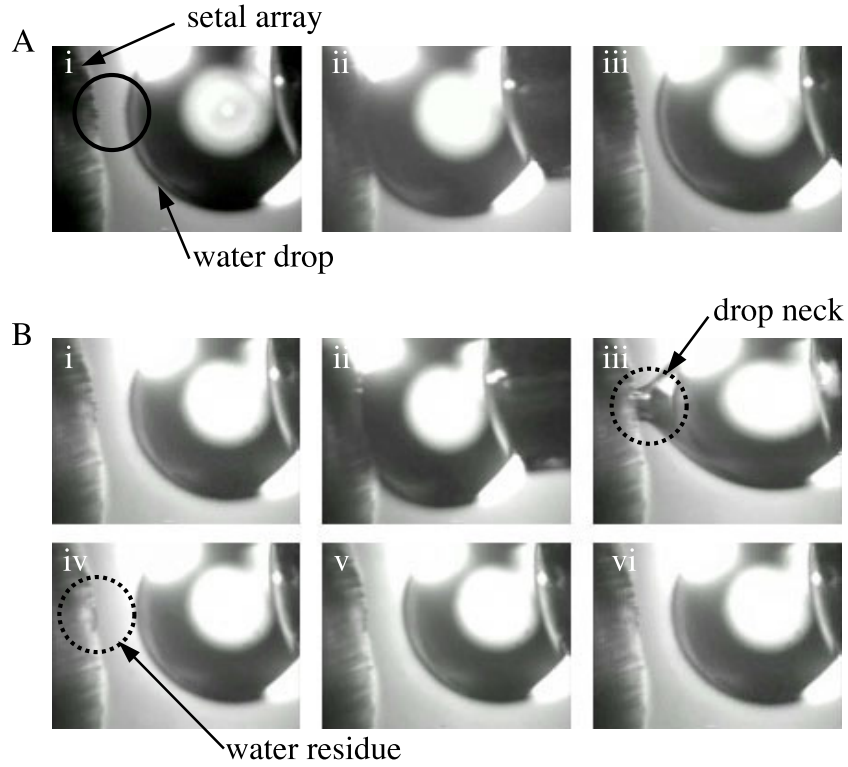
Figure 3. (A) Optical images of a water drop and a setal array (i) before contact, (ii) in contact for 2 s and (iii) after separation. The solid circle in (i) shows the region of the setal array that first contacts the water drop as the surfaces are approached. (B) Optical images of a water drop and a setal array (i) before contact with a setal array that has previously been exposed to water for 20 min, (ii) in contact for 2 s, (iii) after retraction of the water drop from the setal array, (iv, v, vi) after further retraction of the water drop. Experiments were conducted under ambient temperature (23 °C) and humidity (50%).

amount of time (>20 min), the surface proteins within the setal array undergo a conformational change, thereby exposing less hydrophobic domains. This transition results in an overall decrease in the surface hydrophobicity of the setal array and an increase in the surface energy, which leads to an increased adhesion force, consistent with the results obtained by Huber *et al* [20]. The decrease in the adhesion forces of a setal array in an aqueous environment (triangles in figure 4(A)) cannot be explained solely by the fact that capillary contributions are no longer present; the forces obtained in an aqueous environment are drastically lower than the forces obtained in a completely dry environment. However, the results are consistent with the fact the magnitude of the van der Waals forces is diminished. The van der Waals force F_{vdw} between two surfaces interacting between a medium is given by [22]

$$F_{vdw} = \frac{A_{132}R}{6D^2}, \tag{3}$$

where A_{132} is the non-retarded Hamaker constant for a sphere composed of medium 1 (silica surface) and of radius R interacting with a flat surface composed of medium 2 (setal array) across medium 3 (water). The non-retarded Hamaker constant can be estimated on the basis of the Lifshitz theory [30], where

$$A_{132} \approx \frac{3}{2}kT\left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}}$$
$$\times \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2}[(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}]} \tag{4}$$

where ε_1, ε_2 and ε_3 are the dielectric constants, n_1, n_2 and n_3 are the refractive indices for silica, the setal array and water, respectively, h is Planck's constant and ν_e is the absorption frequency in the UV which is around 3×10^{-15} s^{-1}. Using typical values (see table 1) for the dielectric constants of silica, the setal array (values for polystyrene are used) and water, the Hamaker constant for the setal array interacting with a silica surface in water $A_{132,water} = 9.64 \times 10^{-21}$ J. For similar surfaces interacting in air (or vacuum), the Hamaker constant is $A_{132,air} = 7.08 \times 10^{-20}$ J; a factor of 7.34 larger compared to the surfaces interacting across water. The theoretical decrease in the adhesion force is in good agreement with our experimental results (the adhesion force between the surfaces in air is three times larger compared to when in water) considering the fact that we do not know the exact dielectric constant and refractive index of β-keratin and we do not consider potential ionic interactions between the silica surface and the setal array. In addition, hydrophobic interactions [31] between the setal array and the silica surface would also increase the total adhesion force, which is not considered in equation (4). Furthermore, preliminary data from the Autumn group show that an increase in humidity promotes plastic deformation in setal keratin, which should enhance adhesion. A detailed study of the effect of humidity on the mechanical properties of gecko setae is in progress in the Autumn group.

Figure 4(B) shows the friction force of the highly textured setal array against a silica surface in the gripping direction as the load L is increased. The friction force does not appear to be
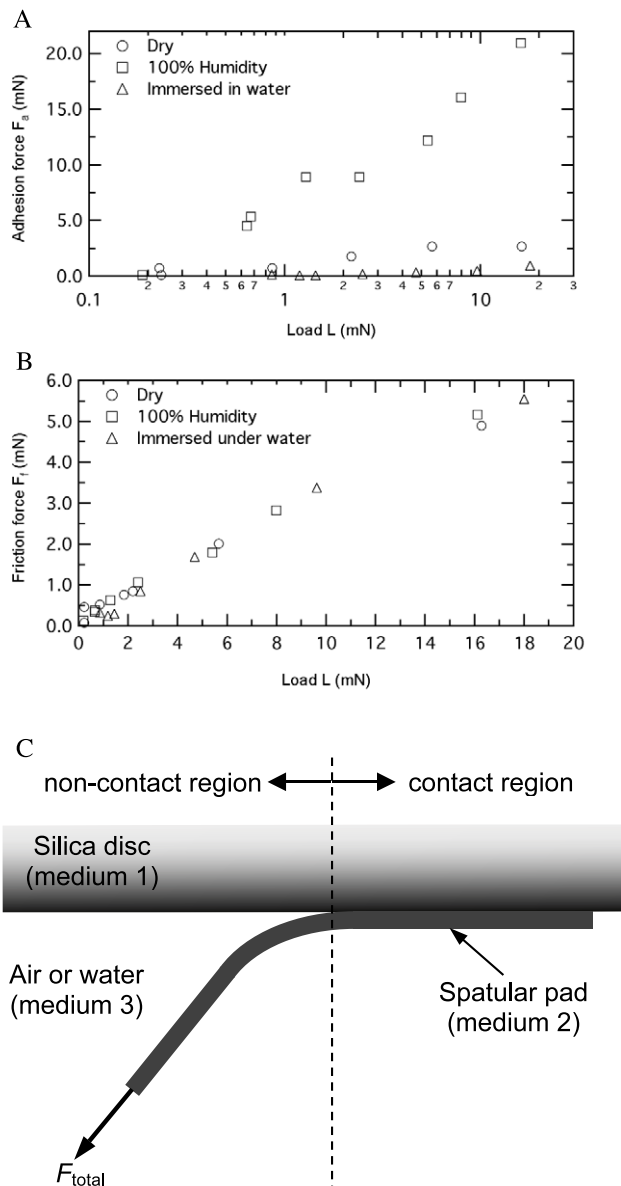
A

B

C

Figure 4. (A) Adhesion F_a and (B) friction F_f forces between a setal array and a silica surface under dry (○ data points), 100% humidity (□ data points) and deionized water (△ data points) as a function of the load L. The contact area between the setal array and the silica surface increases with increasing load, reaching a maximum of approximately 1.5 mm^2 at the highest load (corresponding approximately to a 40 μm normal displacement into the setal array). (C) Schematic illustration of contact and non-contact regions of a spatula pad interacting with a silica surface across a medium. A pulling force F_{total} is exerted on the spatula stalk.

influenced by the environmental conditions under the relatively high loads ($L > 3$ mN), resulting in a friction coefficient of approximately 0.3. These results can be explained by considering the non-contact and contact regions of a spatula pad interacting with a silica surface across a medium as shown schematically in figure 4(C). In the non-contact or 'peel zone' [2, 10] region, where the adhesion force F_a originates, the surfaces interact with each other across the medium (either air or water). In contrast, the friction force F_f originates in the contact region which, at high loads, results

Table 1. Dielectric constants and refractive indices for silica, polystyrene and water [22].

Material	Dielectric constant ε	Refractive index n
Silica	3.8	1.448
Polystyrene	2.55	1.557
Water	80	1.333

in 'load-controlled' [32] as opposed to 'adhesion-controlled' friction and therefore remains unaffected by the different environmental conditions used in this study.

4. Conclusion

The change in surface wetting properties of a tokay gecko setal array was studied when exposed to water. It was found that, upon exposure to water, a change in the hydrophilic–lyophilic balance of the surface of the setal array leads to a conformational change in the surface proteins. The exposed region of the setal array becomes less hydrophobic. SFA experiments were conducted to measure the adhesion and friction forces under varying environmental conditions. The adhesion forces increased with humidity due to an increase in the surface energy and decreased when immersed under water due to a decrease in the van der Waals interactions compared to dry conditions. By contrast, the 'load-controlled' friction forces remained unaffected by the environmental conditions.

References

[1] Autumn K *et al* 2000 *Nature* **405** 681
[2] Pesika N S *et al* 2007 *J. Adhes.* **83** 383
[3] Autumn K *et al* 2002 *Proc. Natl Acad. Sci.* **99** 12252
[4] Ruibal R and Ernst V 1965 *J. Morphol.* **117** 271
[5] Yao H and Gao H 2006 *J. Mech. Phys. Solids* **54** 1120
[6] Autumn K *et al* 2006 *J. Exp. Biol.* **209** 3558
[7] Greiner C, Arzt E and del Campo A 2009 *Adv. Mater.* **21** 479
[8] Chen J J *et al* 2006 *J. Exp. Biol.* **209** 249
[9] Autumn K *et al* 2006 *J. Exp. Biol.* **209** 260
[10] Tian Y *et al* 2006 *Proc. Natl Acad. Sci.* **103** 19320
[11] Geim A K *et al* 2003 *Nat. Mater.* **2** 461
[12] Northen M T 2005 *Nanotechnology* **16** 1159
[13] Murphy M P, Aksak B and Sitti M 2009 *Small* **5** 170
[14] Qu L T *et al* 2008 *Science* **322** 238
[15] Del Campo A, Greiner C and Arzt E 2007 *Langmuir* **23** 10235
[16] Lee J *et al* 2008 *J. R. Soc. Interface* **5** 835
[17] Schubert B *et al* 2008 *J. R. Soc. Interface* **5** 845
[18] Parness A *et al* 2009 *J. R. Soc. Interface* at press
        (doi:10.1098/rsif.2009.0048)
[19] Lee H, Lee B L and Messersmith P 2007 *Nature* **448** 338
[20] Huber G *et al* 2005 *Proc. Natl Acad. Sci.* **102** 16293
[21] Sun W *et al* 2005 *Biophys. J.* **89** L14

[22] Israelachvili J N 1991 *Intermolecular and Surfaces Forces* 2nd edn (London: Elsevier Academic)
[23] Evans F N and Wennerstrom H 1999 *The Colloidal Domain* 2nd edn (New York: Wiley–VCH)
[24] Leckband D *et al* 1993 *Biotechnol. Bioeng.* **42** 167
[25] Luengo G *et al* 1997 *Macromolecules* **30** 2482
[26] Zhao B *et al* 2007 *Langmuir* **24** 1517
[27] Nosonovsky M and Bhushan B 2007 *Nano Lett.* **7** 2633
[28] Dorrer C and Ruhe J 2008 *Langmuir* **24** 1959
[29] Autumn K and Hansen W 2006 *J. Comput. Physiol.* A **192** 1205
[30] Lifshitz E M 1956 *Sov. Phys.—JETP* **2** 73
[31] Leckband D and Israelachvili J 2001 *Q. Rev. Biophys.* **34** 105
[32] Ruths M and Israelachvili J 2008 *Nanotribology and Nanomechanics: an Introduction* 2nd edn, ed B Bhushan (Berlin: Springer)