Key Concepts for section IV (Electrokinetics and Forces)

1: Debye layer, Zeta potential, Electrokinetics

2: Electrophoresis, Electroosmosis

3: Dielectrophoresis

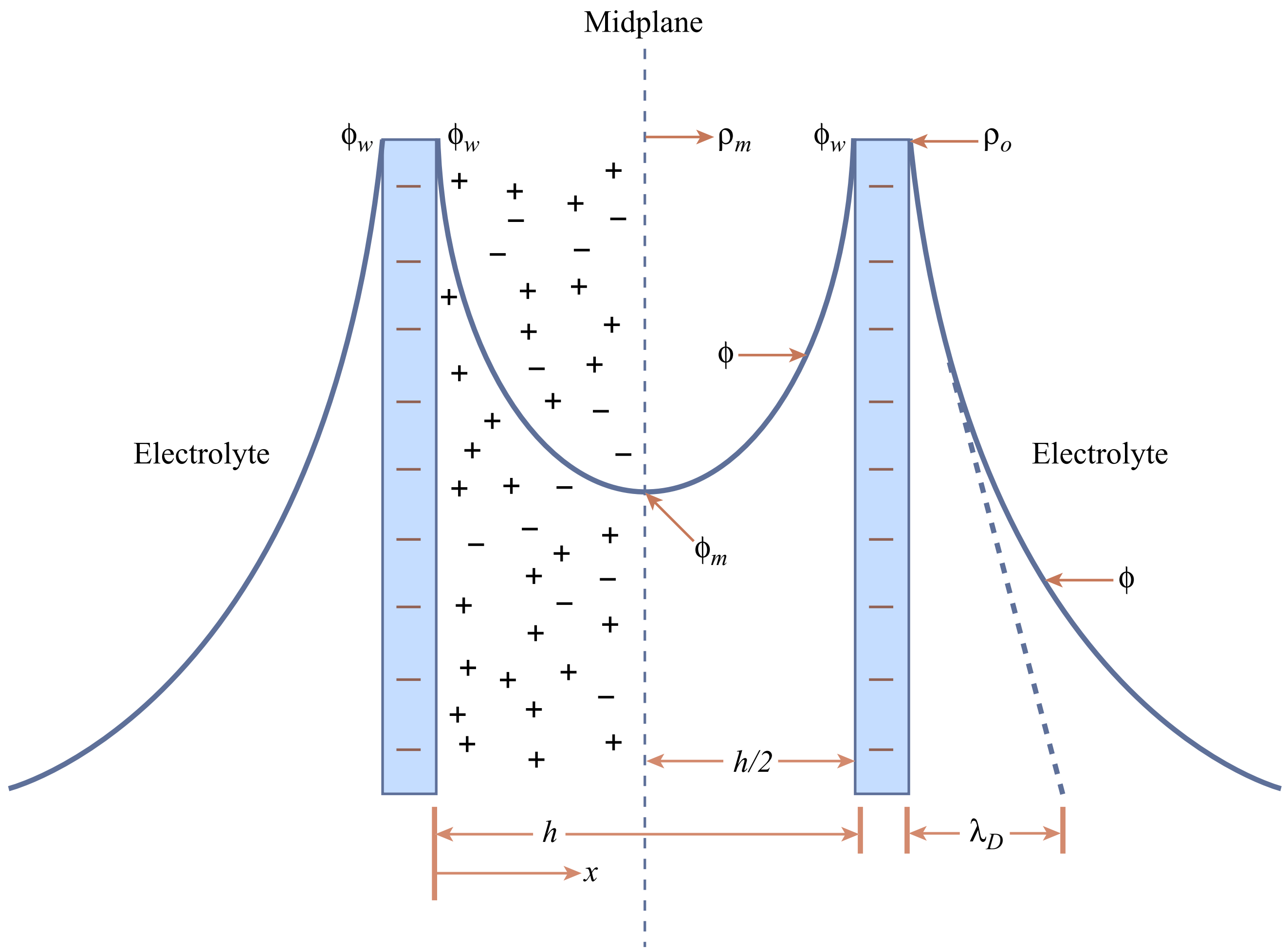
4: **Inter-Debye layer force**, **Van-Der Waals force**

5: Coupled systems, Scaling, Dimensionless Numbers

Goals of Part IV:

(1) Understand electrokinetic phenomena and apply them in (natural or artificial) biosystems

(2) Understand various driving forces and be able to identify dominating forces in coupled systems



Potential distribution resulting from the overlap of double layers from opposing plates.

Figure by MIT OCW.

Values of Hamaker Constants		
Material	$\frac{A_{11}\ (microscopic)}{10^{-20}\ \mathrm{J}}$	$\frac{A_{11}\ (macroscopic)}{10^{-20}\ \mathrm{J}}$
Water	3.3 - 6.4	3.0 - 6.1
Ionic Crystals	15.8 - 41.8	5.8 - 11.8
Metals	7.6 - 15.9	22.1
Silica	50	8.6
Quartz	11.0 - 18.6	8.0 - 8.8
Hydrocarbons	4.6 - 10	6.3
Polystyrene	6.2 - 16.8	5.6 - 6.4

Figure by MIT OCW.

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Tokay Gecko (*Gekko gecko*)

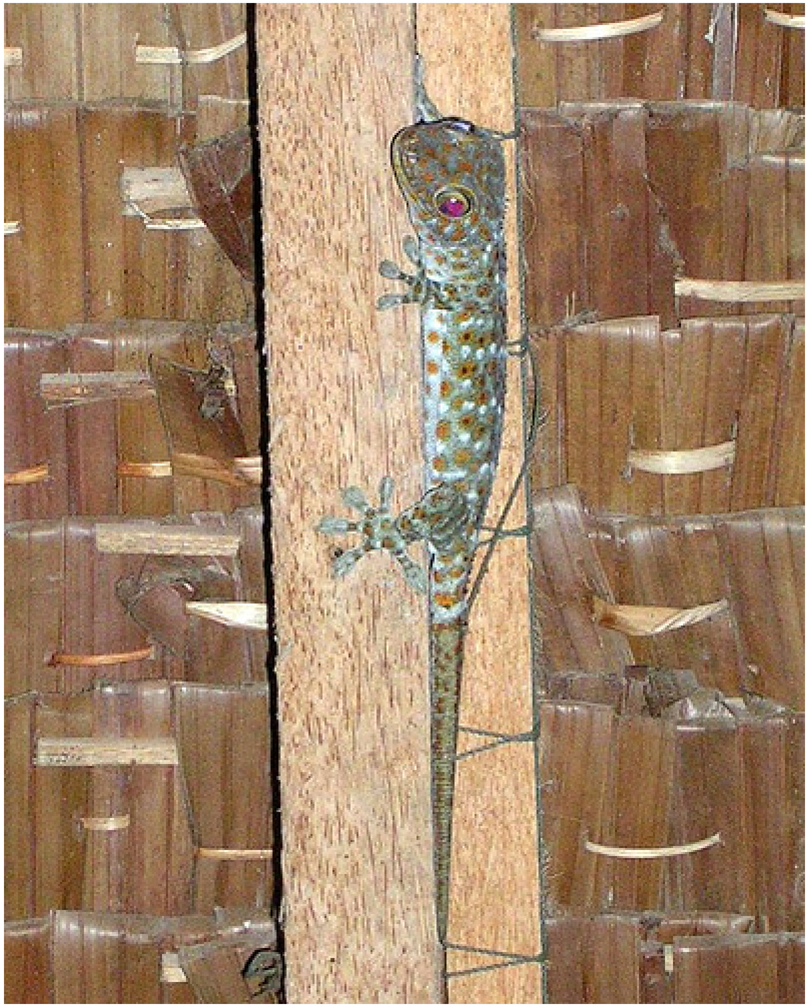


Photo courtesy of ‘elbisreverri’.
http://www.flickr.com/photos/elbisreverri/53226345/

Photo courtesy of David Clements.

Tokay gekco (*Gekko gecko*) has amazing feet……

A lizard from southeast Asia which…..

- can generate ~10 N of adhesive force.
- can run up to ~ 1m /s
- can generate sheer stress of ~0.1N mm^{-2} (~1 atm)
- can walk on ANY surfaces (hydrophobic/hydrophillic/rough/smooth/charged/uncharged…)

What is the mechanism for such an amazing adhesion?

- micro-suction?	No, adhesion works in vacuum.
- friction?	No, measured friction constant too low
- micro-interlocking?	No, it walks on very smooth surface.
- capillary force?	No, it walks on hydrophobic surface.
- charge-interaction?	No, it walks in ionized air.
- adhesion by glue?	No, there are no skin glands on their feet.

K. Autumn et al., Nature, **405**, 681 (2000)

Fig. 2. Tokay gecko (*Gekko gecko*) adhering to molecularly smooth hydrophobic GaAs semiconductor. The strong adhesion between the hydrophobic surface of the gecko's toes and the hydrophobic GaAs surfaces demonstrates that the mechanism of adhesion in geckos is van der Waals force.

Source: Autumn, K., et al. "Evidence for Van der Waals Adhesion in Gecko Setae." *PNAS* 99, no. 19 (September 17, 2002): 12252-12256.

K. Autumn et al., PNAS, **99**, 12252 (2002)

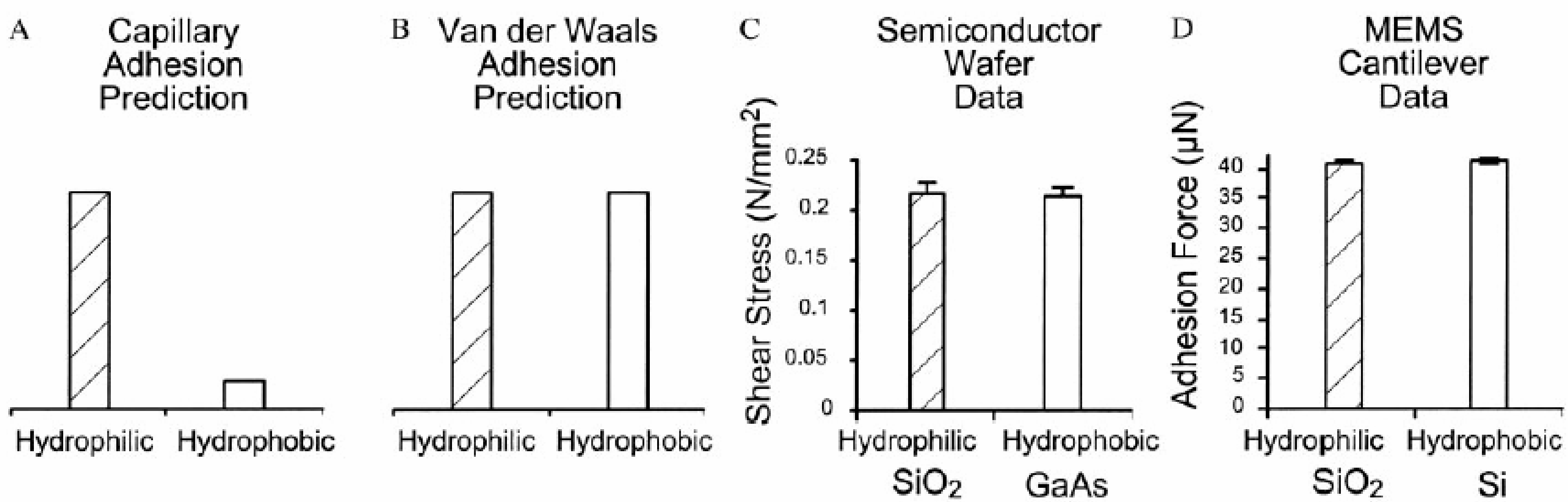
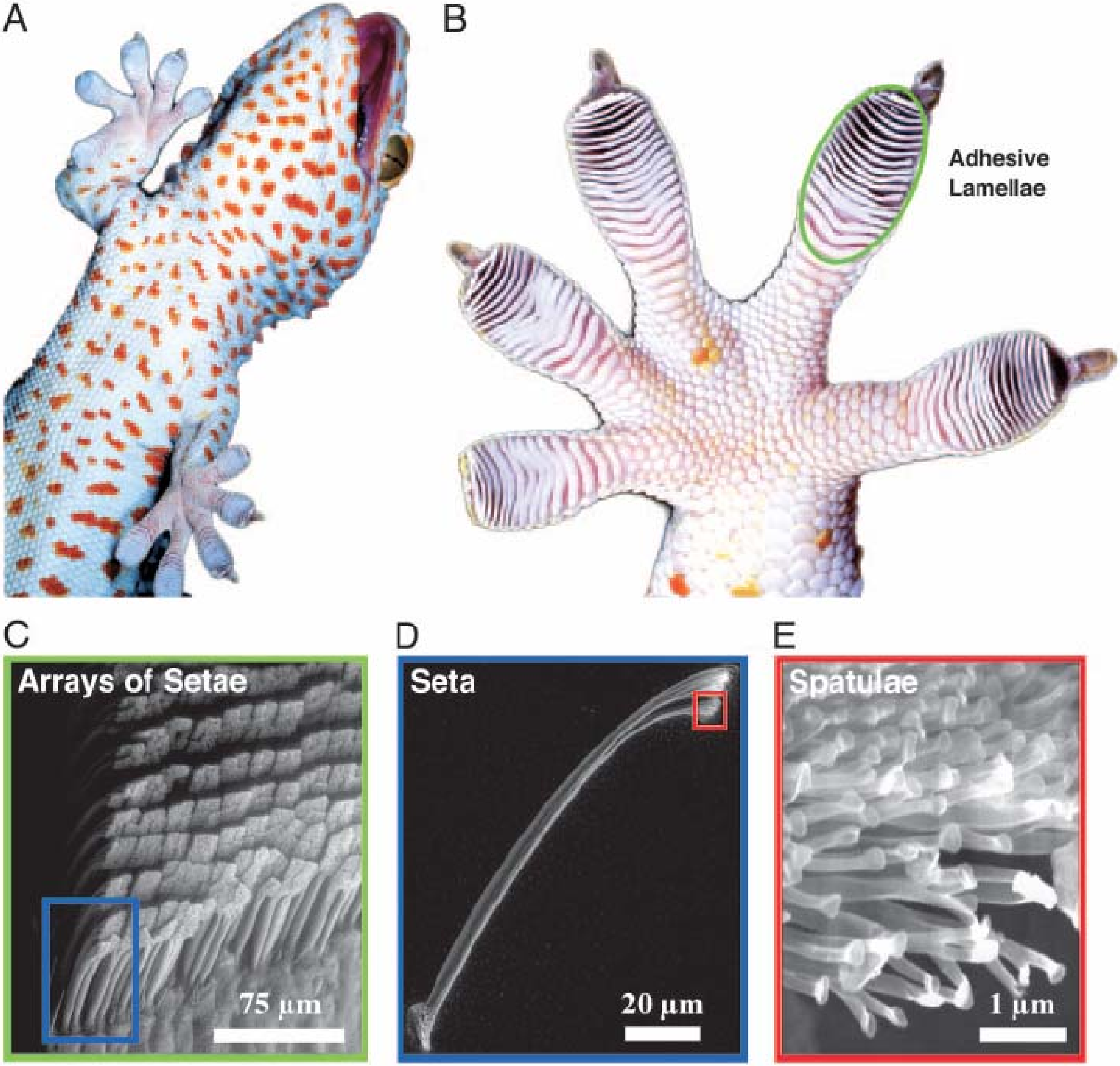


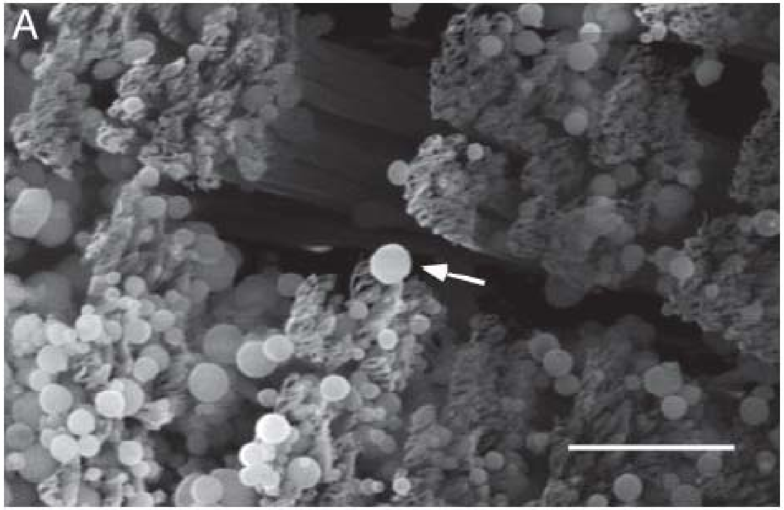
Fig. 1. Force of gecko setae on highly polarizable surfaces versus for surface hydrophobicity. (*A*) Wet adhesion prediction. (*B*) van der Waals prediction. (*C*) Results from toe on highly polarizable semiconductor wafer surfaces differing in hydrophobicity. (*D*) Results from single seta attaching to highly polarizable MEMS cantilevers differing in hydrophobicity. Note that geckos fail to adhere to hydrophobic, weakly polarizable surfaces [polytetrafluoroethylene where $\theta = 105°$ (25) and the dielectric constant, $\varepsilon = 2.0$ (23)]. Adhesion to hydrophilic and hydrophobic polarizable surfaces was similar. Therefore, we reject the hypothesis that wet, capillary interactions are necessary for gecko adhesion in favor of the van der Waals hypothesis.

K. Autumn et al., PNAS, **99**, 12252 (2002)



Source: Autumn, K., et al. "Evidence for Van der Waals Adhesion in Gecko Setae." *PNAS* 99, no. 19 (September 17, 2002): 12252-12256.

W. R. Hansen and K. Autumn, PNAS, **102**, 385 (2005)



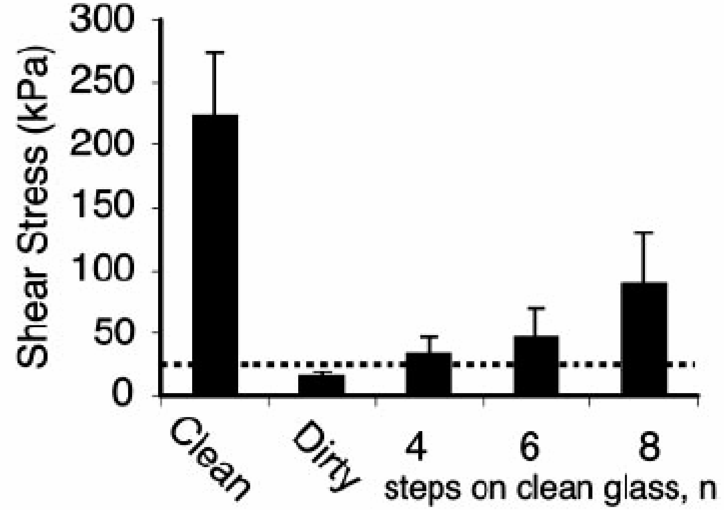


Fig. 3. Mean shear stress in clean, dirty, and self-cleaned gecko digits. Dotted line indicates minimum shear stress required to support one gecko's body weight (43 g) by a single toe (area = 0.19 cm^2). After clogging with >2.5-μm-radius microspheres, four steps on clean glass restored setal force to a level sufficient to support the gecko by a single toe.

W. R. Hansen and K. Autumn, PNAS, **102**, 385 (2005)

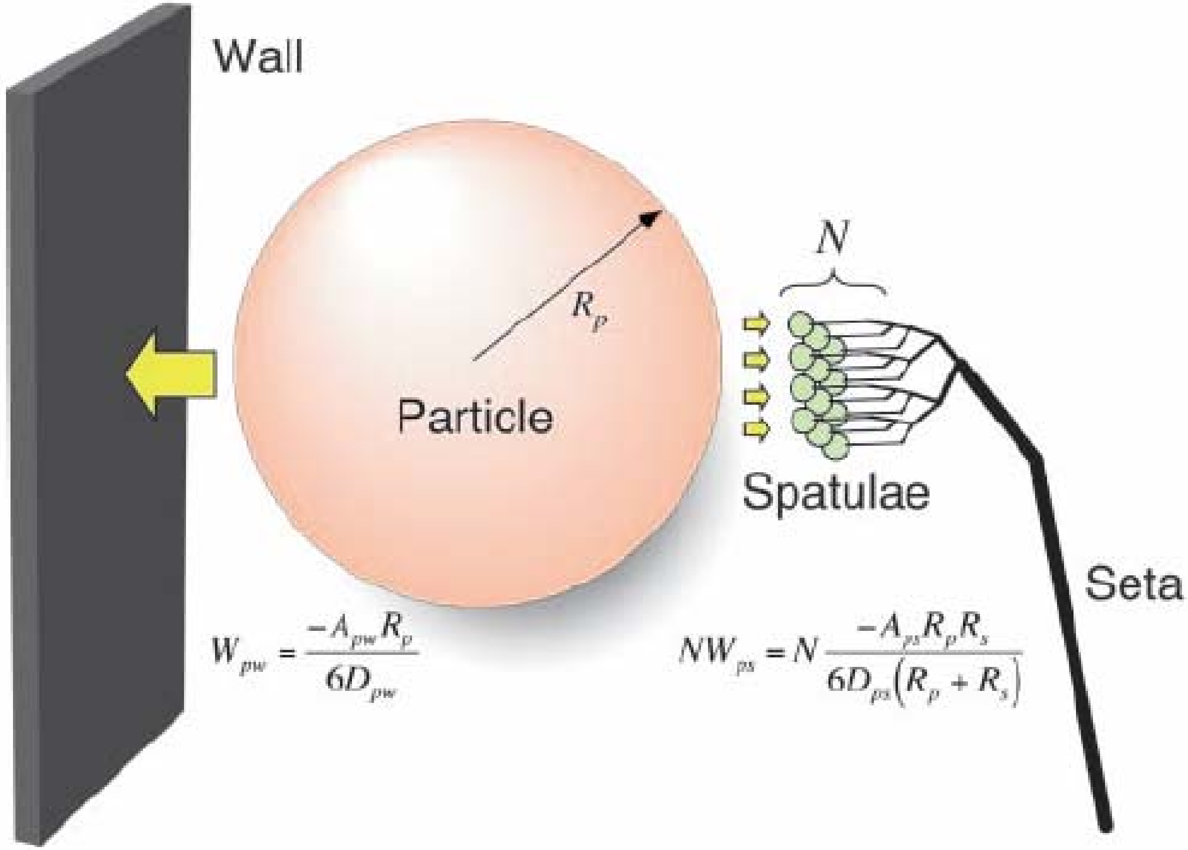
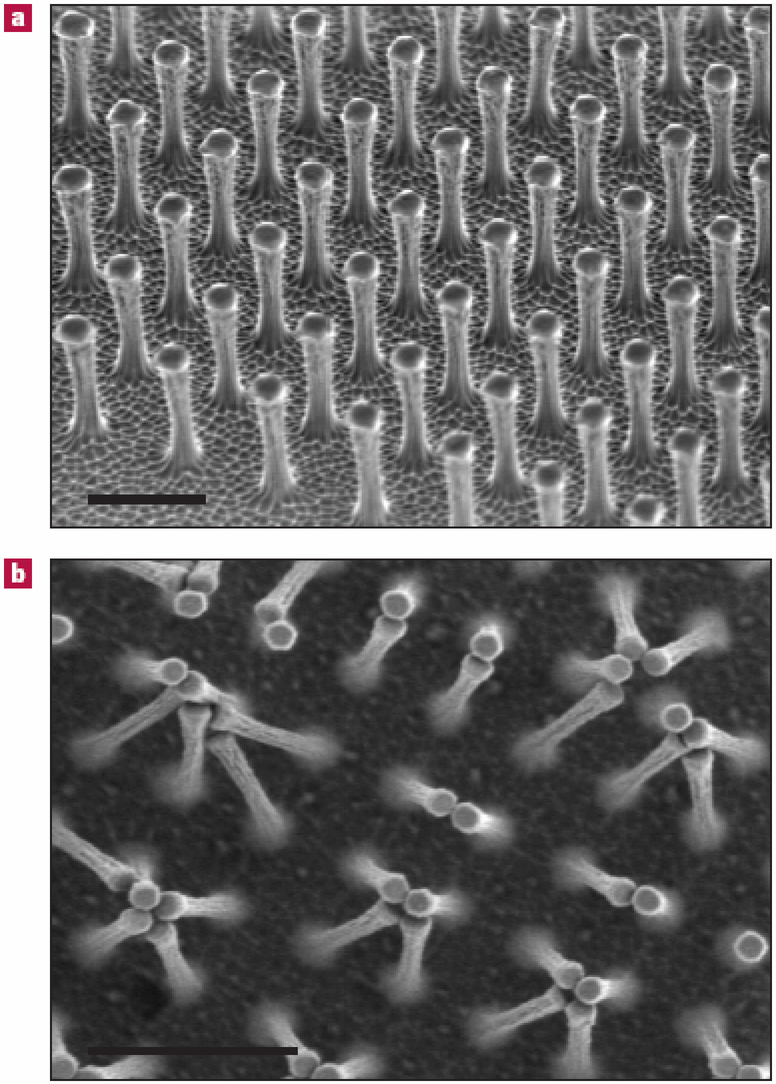


Fig. 5. Model of interactions between N gecko spatulae of radius R_s, a spherical dirt particle of radius R_p, and a planar wall. Van der Waals interaction energies for the particle-spatula (W_{ps}) and particle-wall (W_{pw}) systems are shown. When $N \times W_{ps} = W_{pw}$, equal energy is required to detach the particle from wall or N spatulae. Our results suggest that N is sufficiently great that self-cleaning results from energetic disequilibrium between the wall and the relatively few spatulae that can attach to a single particle.

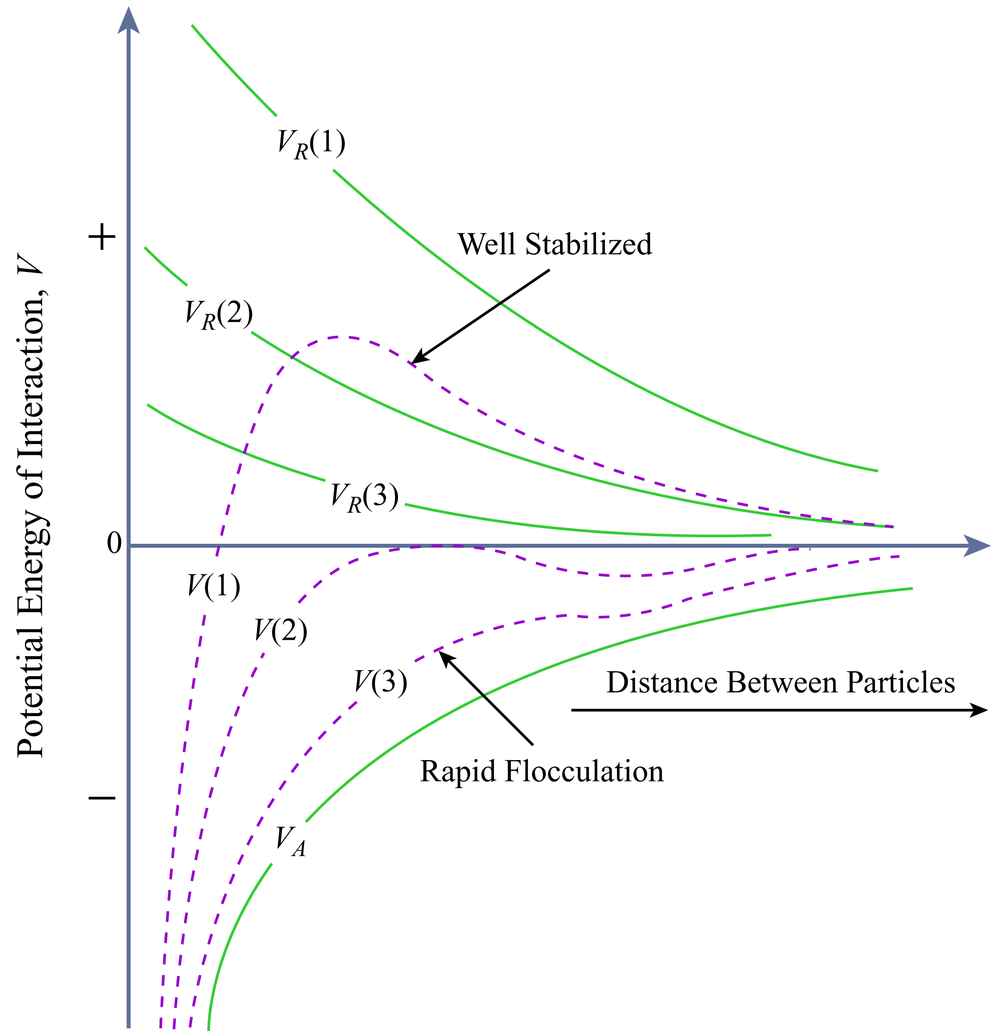
W. R. Hansen and K. Autumn, PNAS, **102**, 385 (2005)



Geim, A. K., et al. "Microfabricated Adhesive Mimicking Gecko Foot-hair." *Nature Materials* 2 (June 1, 2003): 461.

A. K. Geim et al. Nature Materials, **2**, 461 (2003)

Total Interaction Energy Curves



Curves obtained by summation of an attraction curve with various repulsion curves (after Shaw 1980).

Figure by MIT OCW.

Critical coagulation concentrations for hydrophobic solutions (millimoles per dm^3)					
As_2S_3 (-ve sol)		*AgI (-ve sol)*		*Al_2O_3 (+ve sol)*	
LiCl	58	$LiNO_3$	165	NaCl	43.5
NaCl	51	$NaNO_3$	140	KCl	46
KCl	49.5	KNO_3	136	KNO_3	60
KNO_3	50	$RbNO_3$	126		
K acetate	110	$AgNO_3$	0.01		
$CaCl_2$	0.65	$Ca(NO_3)_2$	2.40	K_2SO_4	0.30
$MgCl_2$	0.72	$Mg(NO_3)_2$	2.60	$K_2Cr_2O_7$	0.63
$MgSO_4$	0.81	$Pb(NO_3)_2$	2.43	K_2 oxalate	0.69
$AlCl_3$	0.093	$Al(NO_3)_3$	0.067	$K_3[Fe(CN)_6]$	0.08
$\frac{1}{2}Al_2(SO_4)_3$	0.096	$La(NO_3)_3$	0.069		
$Al(NO_3)_3$	0.095	$Ce(NO_3)_3$	0.69		

Figure by MIT OCW.

From "Introduction to Colloid and Surface Chemistry"
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Figures 8.3 and 8.4: Influence of electrolyte concentration and Stern potential on the total potential energy of interaction of two spherical particles.

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- Fig. 9.10: Apparatus to measure long-range forces between sheets of mica immersed in liquid.
- Fig. 9.11: Graph of double-layer repulsion in the presence of potassium chloride.
- Fig. 9.12: Graph of attractive van der Waals dispersion forces between mica surfaces.

From “ Introduction to Modern Colloid Science”
By Robert J. Hunter (Oxford Science Publications)