Surface Energy
Surface Tension
Wetting
Capillary

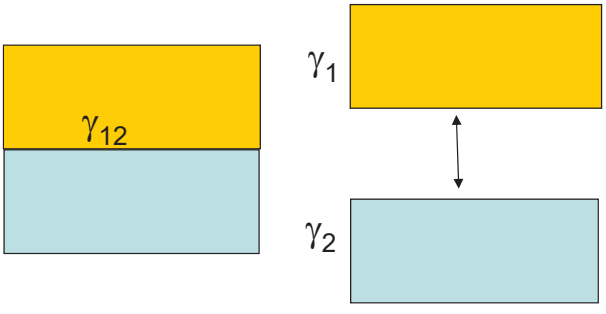
Adhesion and Surface Energy

The energy of adhesion (or just *adhesion*), *W*, i.e., the energy per unit area necessary to separate two bodies (1 and 2)

$W_{12} = 2\gamma_{12}$; $\gamma_{12} \approx \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1 \gamma_2}$

$W_{12} = 2\gamma_{12} \approx \sqrt{\gamma_1}\sqrt{\gamma_2}$

γ_{12} interfacial energy
$\gamma_{1/2}$ surface energy of surface 1 and 2



$$\Delta W = W(D_o) - W(D = \infty) = -\frac{A}{12\pi D_o^{\,2}}$$

$$\gamma_{12} = \frac{A}{24\pi D_o^2}$$ $D_o \sim 0.165$ nm

D_o "universal" contact distance (cutoff distance) for "rigid" material

Surface Energy

Surface energies based on Lifshitz theory and experimental values.
(Source: intermolecular & Surface Forces, J. Israelachvili, Academic Press)

Material	A (10^{-20})	Surface Energy, γ (mJ/m^2) Lifshiz Theory $A/24\pi D_o^2$ {D_o=0.165nm}	Surface Energy, γ (mJ/m^2) Experimental* (20°C)
Liquid helium	0.057	0.28	0.12 - 0.35(at 4-1.6K)
Water	3.7	18	73
Acetone	4.1	20.0	23.7
Benzene	5.0	24.4	28.8
CCl_4	5.5	26.8	29.7
H_2o_2	5.4	26	76
Formamide	6.1	30	58
Methanol	3.6	18	23
Ethanol	4.2	20.5	22.8
Glycerol	6.7	33	63
Glycol	5.6	28	48
n-Pentane	3.75	18.3	16.1
n-Hexadecane	5.2	25.3	27.5
n-Octane	4.5	21.9	21.6
n-Dodecane	5.0	24.4	25.4
Cyclohexane	5.2	25.3	25.5
PTFE	3.8	18.5	18.3
Polystyrene	6.6	32.1	33
Polyvinyl chloride	7.8	38.0	39

$$\gamma = \frac{A}{24\pi D_o^2}$$

Surface Energy Calculations of Solids based on the Sublimation Energy

The surface energy γ is related to the sublimation energy L_s as:

$$\gamma = k\left(\frac{L_S}{N_A^{1/3}}\frac{\rho}{M}\right)^{2/3}$$

ρ … density [kg/m^3]
M …molecular weight per mole [kg]
L_s …sublimiation energy [kJ/mol]
N_A …Avogadro's Number

with the constant $k \approx 0.12$ for solid metal surfaces.
k was estimated to be 0.27 for fcc lattices (i.e., for crystal structures of a coordination difference of 4 atoms or molecules between bulk and surface, and involving only short-range additive interactions.

Surface Energy Calculations of Solids based on the Sublimation Energy

Table: Surface Energy Calculations and Observations of Metals (k = 0.12)

Metal	MP (°C)	L_S (kJ mol^{-1}) at 25 °C	M (kg)	ρ (kg m^{-3})	γ (mJ m^{-2}) Calc.	γ (mJ m^{-2}) Obs.*
Indium	156	240	0.115	7.3×10^3	585	630
Lead	327	200	0.207	11.3×10^3	540	560
Gold	1063	380	0.197	19.3×10^3	1485	1400
Iron	1537	400	0.056	7.9×10^3	1800	2100
Platinum	1769	570	0.195	21.5×10^3	2250	2500
Tungsten	3380	850	0.184	19.3×10^3	3015	2900

* Observed measurements are generally made at elevated temperatures just below the MP. Values of γ increase as the temperature is reduced reaching a maximum at 0 K where γ is 5 to 10 per cent greater than the values quoted in the table. See W. R. Tyson, 'Surface energies of solid metals', *Canadian Metallurgical Quarterly*, vol. 14 (1975), pp. 307–14.
Note: mJ m^{-2} = erg cm^{-2}.

Modified from Source: D. Tabor, *Gases, liquids and solids and other states of matter*, 3rd Ed.., Cambridge Univ. Press (2003)

Surface Tension Calculations of Liquids based on the Latent Heat of Vaporization

In analogy to the solid, the surface tension γ can be related to the heat of vaporization ΔH as:

$$\gamma = k \frac{\Delta H}{N_A^{1/3}} \left(\frac{\rho}{M} \right)^{2/3}$$

ρ … density [kg/m^3]
M …molecular weight per mole [kg]
ΔH …lat. heat of vaporization [kJ/mol]
N_A …Avogadro's Number

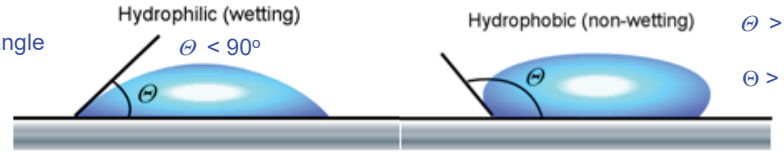
with the constant $k \approx 0.3$.

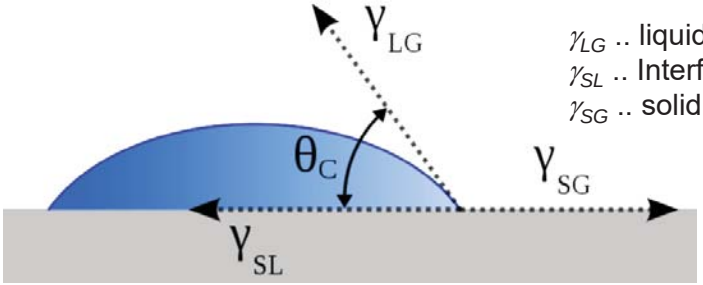
Liquid	Surface Tension [mJ/m^2] calculated	observed
Argon	14	13
Neon	4	5.5
Nitrogen	11	10.5
Oxygen	13	18
Benzene	110	40
Mercury	630	600

Wetting

in the case of water:

Θ … wetting angle





γ_{LG} .. liquid surface tension
γ_{SL} .. Interfacial energy (solid/liq)
γ_{SG} .. solid surface energy

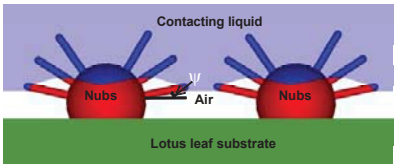
Young's Equation: $\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta$

Dupré Eq.: $\gamma_{12} = \gamma_1 + \gamma_2 - W_{12}$ $W_{12} = \sqrt{\gamma_1 \gamma_2}$ .. adhesion energy per unit area

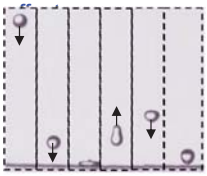
Super - Hydrophobicity:

Lotus Leaf

by Anish Tuteja (MIT)



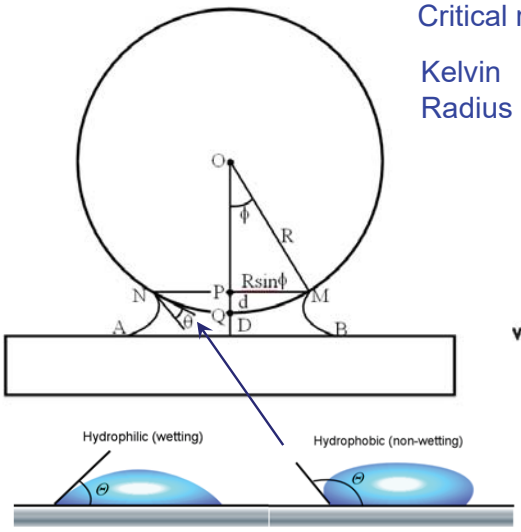
Θ > 150° Lotus



The super-hydrophobicity of the lotus leaf originates from the low surface energy of the wax crystalloids covering the protruding nubs and its surface roughness.

Capillary Forces

Capillary forces are meniscus forces due to third media condensation.



θ the meniscus contact angle

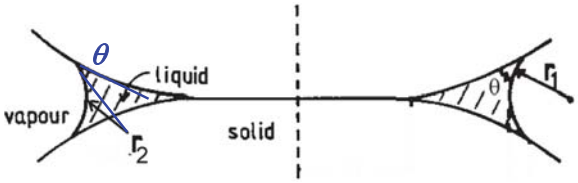
Critical radius for water condensation:

Kelvin Radius

$$r_K = \frac{\gamma_L V}{RT \log\left(\frac{p}{p_s}\right)}$$

γ_L is the surface tension
R the gas constant
p_s saturation vapor pressure

relative humidity

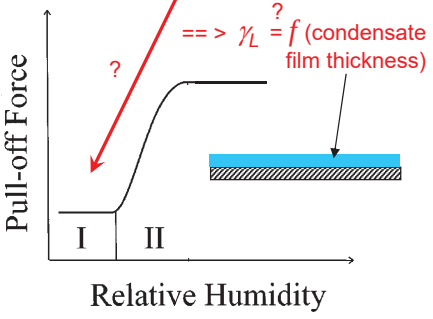


Maximum capillary force, found at at D = 0:

$$F_{max}^{R>>d} = 4\pi R\gamma_L \cos\theta$$

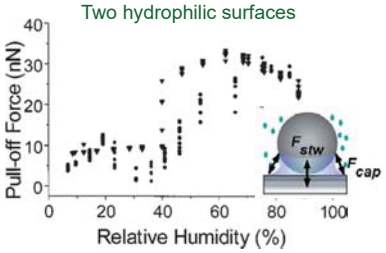
"UNIQUE" Experimental Observation and Model Suggestion for the Nanoscale

$$F_{max}^{R>>d} = 4\pi R\gamma_L \cos\theta$$



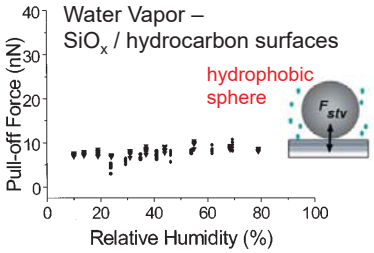
Water Vapor – SiO_x surfaces

Two hydrophilic surfaces



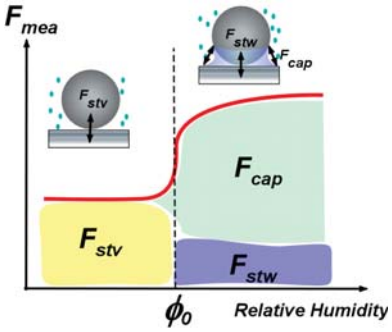
Water Vapor – SiO_x / hydrocarbon surfaces

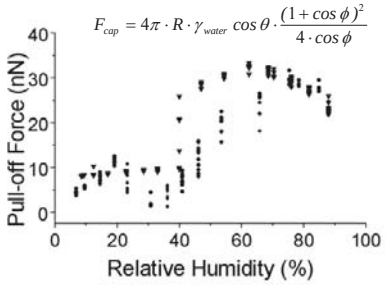
hydrophobic sphere



M. He, R Overney et al., J. Chem. Phys. 114, 1355-1360 (2001).

Capillary Forces





$$F_{cap} = 4\pi \cdot R \cdot \gamma_{water} \cos\theta \cdot \frac{(1+\cos\phi)^2}{4 \cdot \cos\phi}$$

VdW only

RH < 35% $\quad F_{total} = F_{stv} = \dfrac{RA}{24D_o^2}$

Capillary will dominate

RH > 40 % $\quad F_{total} = R\left(\dfrac{A}{24D_o^2} + 4\pi \cdot \gamma_{water} \cos\Theta\right)$

M. He, A. Blum, D. E. Aston, C. Buenviaje, and R. M. Overney, J. Chem. Phys. 114 (3), 1355 (2001)

http://depts.washington.edu/nanolab/NUE_UNIQUE/Lab_Units/3_Lab_Unit_FD.pdf