Special Topics in Physical Chemistry
Colloidal Materials

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Chapter 6

The Solid-Liquid interface

The solid-liquid interface

Lecture objectives and expected outcomes

- To introduce the concept of wetting and its relation to contact angle and wetting
- To identify the different types of wetting: spreading, adhesional, and immersional wetting.
- To derive the physical chemical laws and relations that describe the above wetting processes based on their thermodynamics.
- To explore the applications of wetting process in wetting agents, water repellency, and Detergents.

Competence = knowledge + skills

The solid-liquid interface

Contact angles and wetting

Witting is the displacement from a surface of one fluid by another.

- Example: Air is displaced by a liquid at the surface of a solid.
- Wetting agent is a surface-active substance which promotes this effect.
- Three types of wetting can be distinguished:
  1. *Spreading* wetting.
  2. *Adhesional* wetting.
  3. *Immersional* wetting.

Contact angles and wetting

Spreading wetting

- In spreading wetting: a liquid already in contact with the solid spreads so as
  - to increase the solid-liquid interfacial areas, ΔA (S-L)
  - to increase the liquid-gas interfacial areas, ΔA (L-G) and
  - to decrease the solid-gas interfacial area, ΔA (S-G).
  - **ΔA (S-L)↑, ΔA (L-G)↑, ΔA (S-G)↓**

Contact angles and wetting

Spreading Coefficient

- The spreading coefficient, *S*, is defined by

$$\boldsymbol{S} = - \Delta G_S / A$$

$$= \gamma_{SG} - (\gamma_{SL} + \gamma_{LG}) \qquad \textbf{(1)}$$

where $\Delta G S$ is the free energy increase due to spreading.

- If $\boldsymbol{S}$ **= (+)** values ∴Spontaneous spreading occurs
- If $\boldsymbol{S}$ **= (-)** values ∴the liquid remains as a drop of definite contact angle, θ, with the solid surface.

Consider a liquid making a contact angle, θ, to spread an extra area dA on a solid surface!

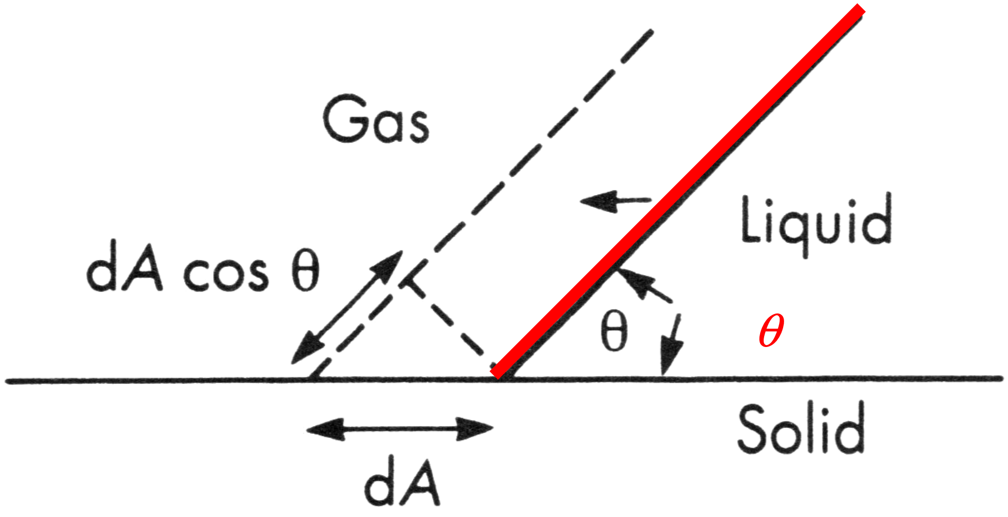
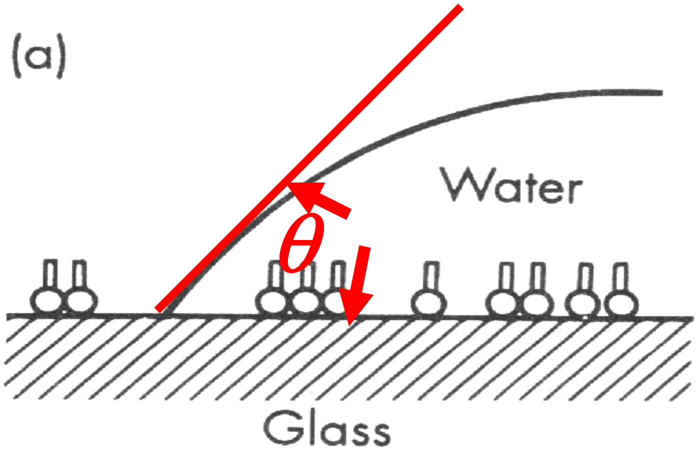


Figure 6.1



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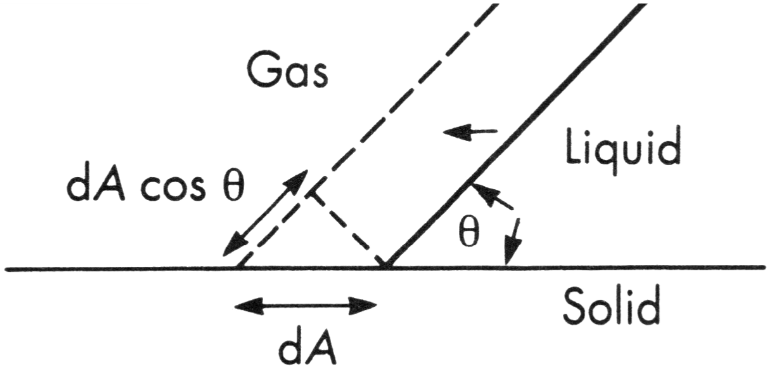

Figure 6.1

- The increase in liquid-gas interfacial area is $dA \cos\theta$
- The increase in the free energy of the

$$\boxed{dG = \gamma_{SL}\, dA + \gamma_{LG}\, dA \cos\theta - \gamma_{SG}\, dA}$$

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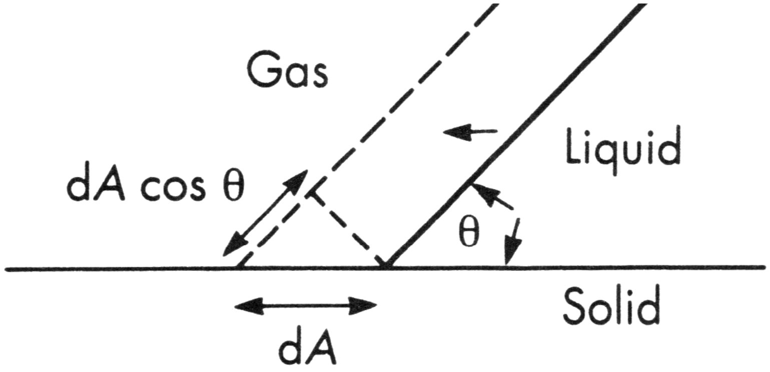

Figure 6.1

- The increase in liquid-gas interfacial area is $\mathrm{d}A \cos\theta$
- The increase in the free energy of the

$$dG = \gamma_{\mathrm{SL}}\, dA + \gamma_{\mathrm{LG}}\, dA \cos\theta - \gamma_{\mathrm{SG}}\, dA$$

  - At equilibrium $\mathrm{d}G = 0$, and

$$\gamma_{\mathrm{SL}} + \gamma_{\mathrm{LG}} \cos\theta - \gamma_{\mathrm{SG}} = 0 \qquad (2)$$

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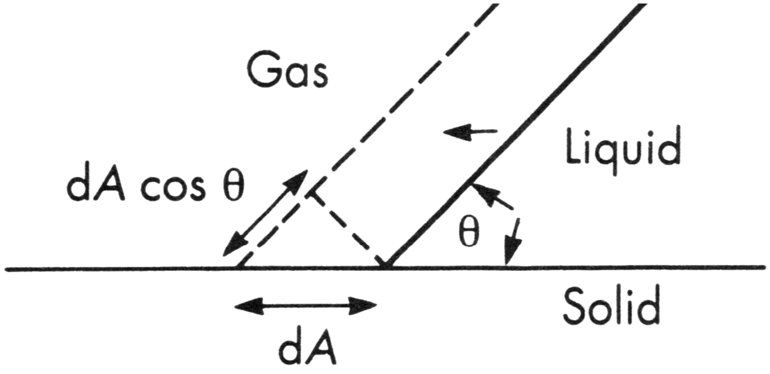


Figure 6.1

- The increase in liquid-gas interfacial area is $dA \cos\theta$
- The increase in the free energy of the system is given by

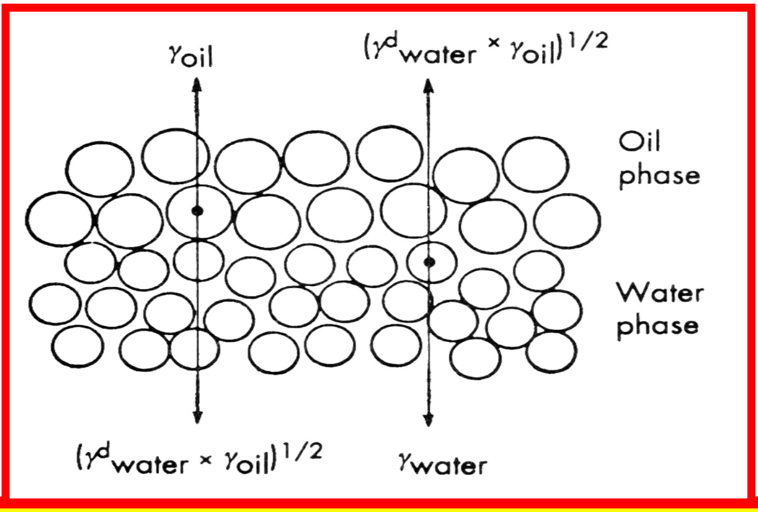
$$\boxed{dG = \gamma_{SL}\, dA + \gamma_{LG}\, dA \cos\theta - \gamma_{SG}\, dA}$$

  - At equilibrium $dG = 0$, and

$$\boxed{\gamma_{SL} + \gamma_{LG} \cos\theta - \gamma_{SG} = 0 \qquad (2)}$$

- Eq 2 known as Young’s eq

γ_{SL} [redacted]ing Fowkes' semiempirical interfacial tension theory.



$$\gamma_{SL} = \gamma_{S} + \gamma_{LG} - 2(\gamma_{S}^{d} \times \gamma_{LG}^{d})^{1/2}$$

$$\gamma_{\mathrm{SL}} + \gamma_{\mathrm{LG}} \cos\theta - \gamma_{\mathrm{SG}} = 0 \qquad (2)$$

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{S}} + \gamma_{\mathrm{LG}} - 2(\gamma_S^d \times \gamma_{LG}^d)^{1/2}$$

- From the above two equations we can get

$$\cos\theta = -1 + \frac{2(\gamma_S^d \times \gamma_{LG}^d)^{1/2}}{\gamma_{LG}}$$

- Note that $\gamma_S \approx \gamma_{SG}$ in the above case

$$\cos\theta = -1 + \frac{2(\gamma_S^d \times \gamma_{LG}^d)^{1/2}}{\gamma_{LG}}$$

- For non polar liquid;

$$\gamma_{LG}^d = \gamma_{LG}$$

$$\cos\theta = -1 + 2(\gamma_S^d / \gamma_{LG})^{1/2} \qquad (6)$$

- When cos θ = -1 , θ = 180° no spreading
- When cos θ = 1 , θ = 0° complete spreading
- i.e. θ should decrease as γ_{LG} decreases
- θ =0 below a certain value of γ_{LG}
- this γ_{LG} is named as critical surface tension

critical surface tension

- *Critical surface tension is a useful parameter for characterizing the wettability of a solid surface*

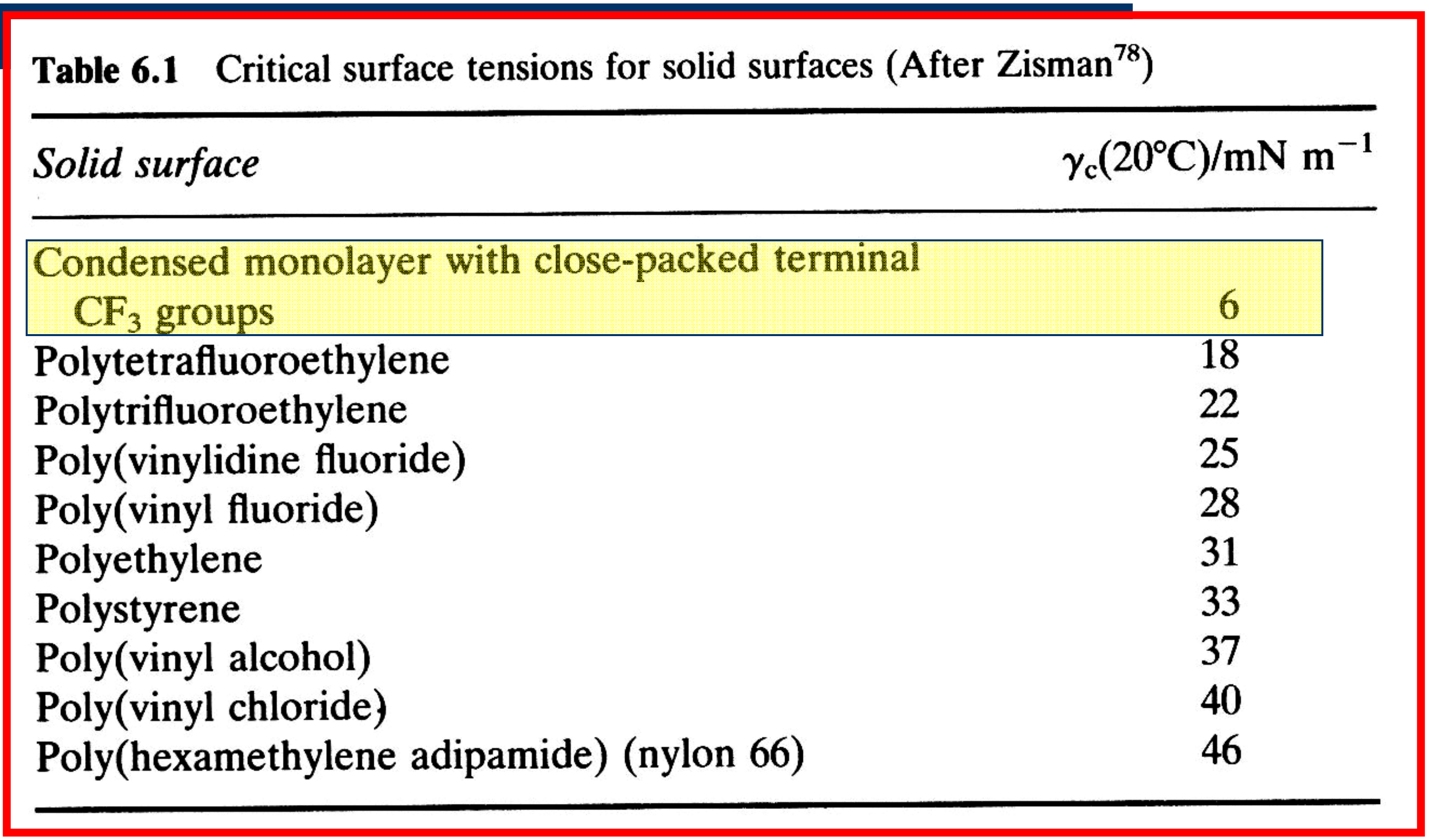


Table 6.1 Critical surface tensions for solid surfaces (After Zisman[78])

Solid surface	γ_c(20°C)/mN m^{-1}
Condensed monolayer with close-packed terminal CF_3 groups	6
Polytetrafluoroethylene	18
Polytrifluoroethylene	22
Poly(vinylidine fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Poly(vinyl chloride)	40
Poly(hexamethylene adipamide) (nylon 66)	46

Contact angles and wetting

Adhesional wetting

- **In adhesional wetting: a liquid which is not originally in contact with the solid substrate makes contact and adheres to it.**

- **This leads to**
  - ΔA (S-L)↑, ΔA (L-G) ↓, ΔA (S-G)↓

Contact angles and wetting

The work of adhesion

$$W_a = -\Delta G_a / A$$

$$W_a = \gamma_{SG} + \gamma_{LG} - \gamma_{SL} \qquad (7)$$

- *Com*

$$\gamma_{\mathrm{SL}} + \gamma_{\mathrm{LG}} \cos\theta - \gamma_{\mathrm{SG}} = 0 \qquad (2)$$

$$W_a = \gamma_{LG}(1 + \cos\theta) \qquad (8)$$

- ***Contact angle θ = Zero, when cos θ =1,***
- ***then Wa = $2\gamma_{LG}$ = Wc***
- ***Liquid-Solid attraction ≥ Liquid-Liquid attraction***

Contact angles and wetting

Immersional wetting

- In immersional wetting, the solid, which is not in originally in contact with the liquid , is immersed completely in the liquid.

- This leads to
  - the liquid-gas interfacial areas remains unchanged, and
  - ΔA (S-L)↑, ΔA (S-G)↓

Contact angles and wetting

Free energy of immersion

$$-\Delta G_i = \gamma_{SG} - \gamma_{SL}$$

- *Combination with Young's equation*

$$\gamma_{SL} + \gamma_{LG}\cos\theta - \gamma_{SG} = 0 \qquad (2)$$

$$-\Delta G = \gamma_{LG}\cos\theta \qquad (9)$$

- *If $\gamma_{SG} > \gamma_{SL}$, then $\theta < 90°$ $\therefore$ immersion is spontaneous*
- *If $\gamma_{SG} < \gamma_{SL}$, then $\theta > 90°$ $\therefore$ work must be done to immerse the solid*

Summary

Factors affecting contact angles and wetting

The three types of wetting are summarized by the following equations:

- $-\Delta G_{spreading} / A = S = \gamma_{SG} - \gamma_{SL} - \gamma_{LG}$
- $-\Delta G_{adhesion} / A = Wa = \gamma_{SG} - \gamma_{SL} + \gamma_{LG}$
- $-\Delta G_{immersion} / A = \gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta$

- ***A reduction of γ_{SL} facilitates all of these processes***

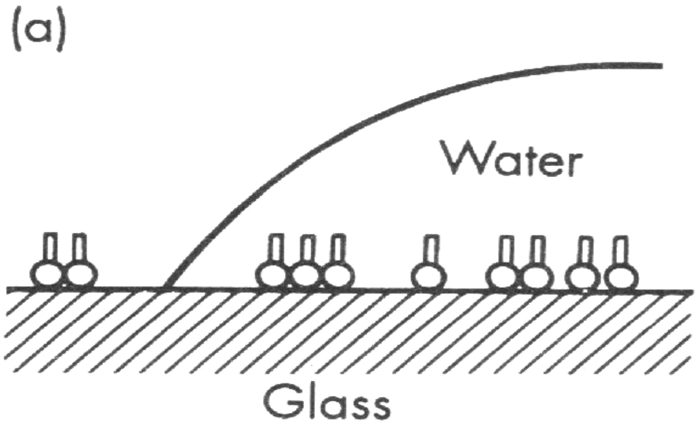
Examples

http://www.howstuffworks.com/

Examples & Applications

Water – glass interaction

- The *contact angle* between water and glass is increased considerably by even less than an adsorbed monolayer of greasy material such as fatty acid.

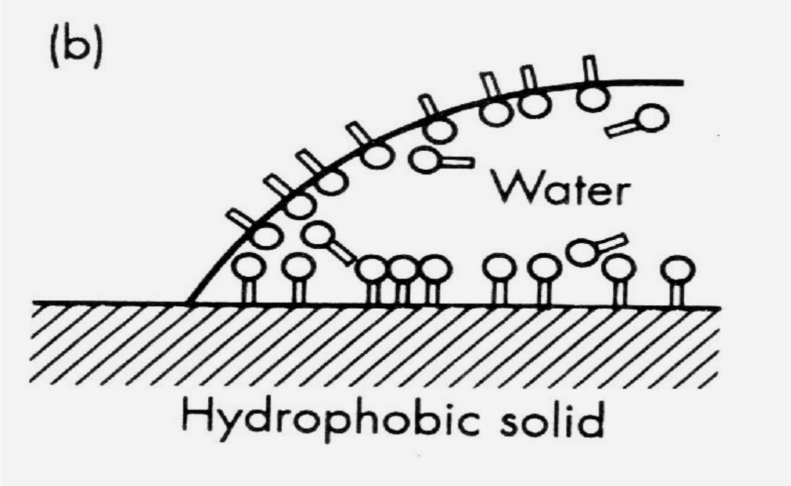


- *Wa is decreased,, θ increases*.

Examples & Applications

***Wetting of a hydrophobic* solid surface**

- The *wetting of a hydrophobic* solid surface by an aqueous medium is considerably helped by the addition of surface-active agents.
- *Wa* is increased, and γ_{LG} is decreased, hence, θ is reduced.



Examples & Applications

Fluorocarbon surfaces

- *Fluorocarbon surfaces* have *low critical surface tensions* (see Table 6.1) and have found well-known application in the production of *'non-stick'* surfaces.
- Fluorocarbon surfaces show much more pronounced non-wetting characteristics, than the corresponding hydrocarbon surfaces, due to the large size of the —CF_2— groups compared with that of the —CH_2— groups.
- Since fewer —CF_2— groups than —CH_2— groups can be packed into a given area of the solid surface, *Wa is less and θ is greater* for the fluorocarbon surface.

Examples & Applications

Wetting agents

- ***SAS** particularly anionics, are used as wetting agents in many practical situations:*
  - *Dips for sheep and cattle.*
  - *Application of insecticide and sprays.*
- *The surfaces in question tend to be greasy or wax-like (unfavourable conditions for surface coverage) unless a wetting agent is incorporated.*
- *However, complete wetting is not desirable either, since it causes over-efficiency in the drainage of excess liquid from the surface.*

Examples & Applications
Water Repellency

- *This is the converse of the previous topic, the aim is to make θ as large as possible.*

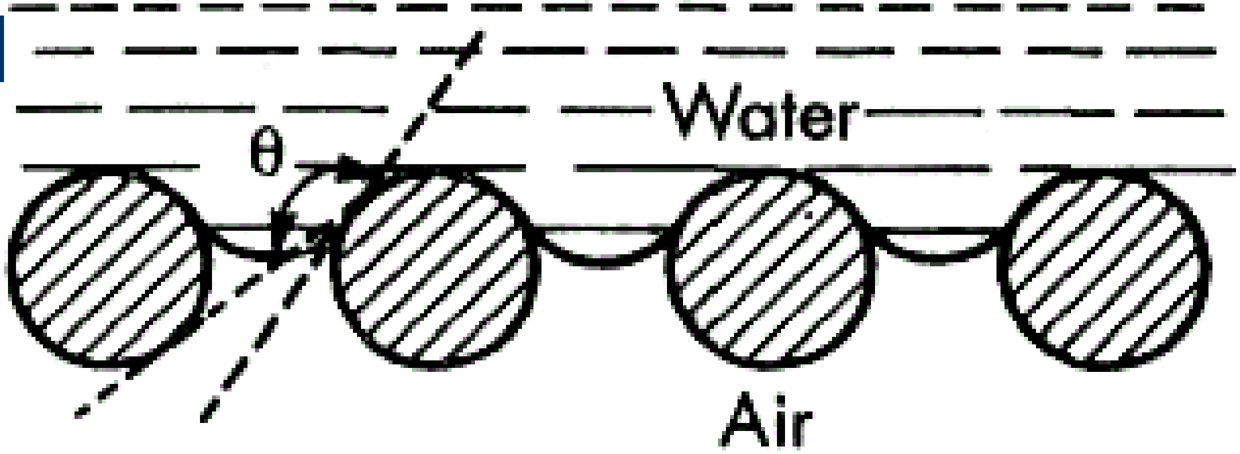
Textile fabrics are made water-repellent by treatment with a long-chain cationic surfactant e.g. stear-amidomethylpyridinium chloride,

$$C_{17}H_{35}CONHCH_2N^+C_2H_5Cl^-$$

- The *pressure required* to force water through the fabric depends on the surface tension and inversely on the fiber spacing, so that a moderately tight weave is desirable.

Examples & Applications

Water Repellency



- *A moderately tight weave is desirable but the passage of air through the fabric is not hindered.*

Examples & Applications

Water Repellency

- *Ducks owe their water-repellent characteristics to the nature of their feathers: wax-covered barbules c. 8 μm in diameter, separated by air gaps of c. 30 μm.*

- *Dimethyldichlorosilane, is a very good hydrophobising agent for silica and glass surfaces; it reacts with the —OH groups on the outside of the silicate lattice*

$$2(\equiv\text{Si-OH}) + (\text{Cl})_2\text{Si}(\text{CH}_3)_2 \rightarrow (\equiv\text{Si-O})_2\text{Si}(\text{CH}_3)_2$$