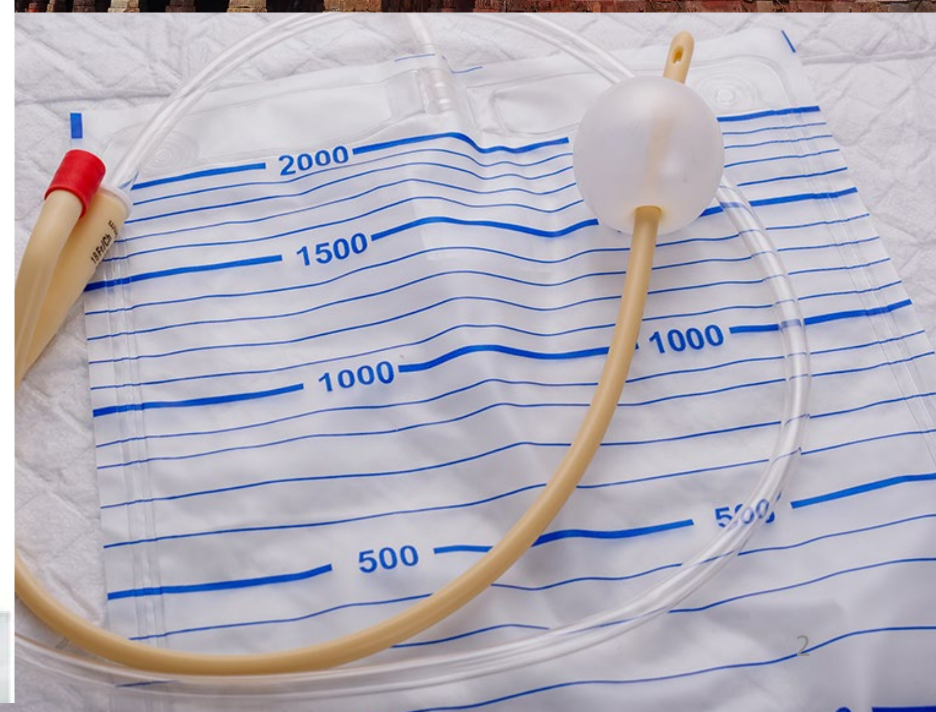
# Introduction to

# Surfaces and Interfaces

# Outline

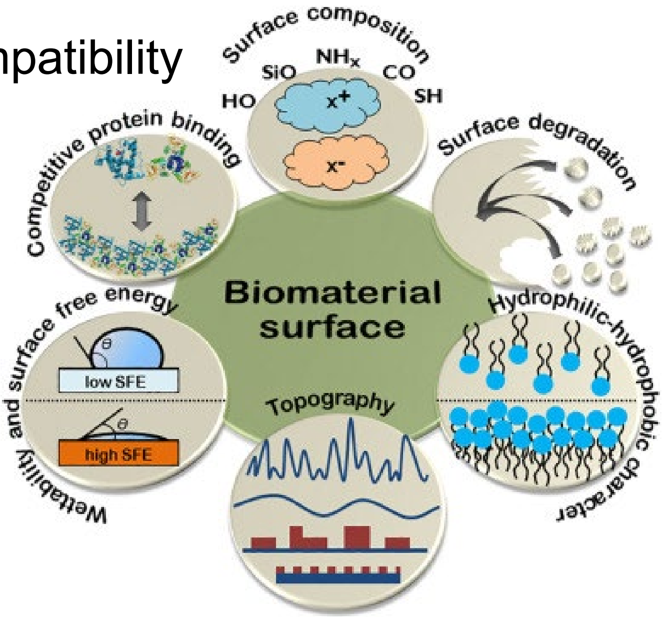


# Why study surfaces?

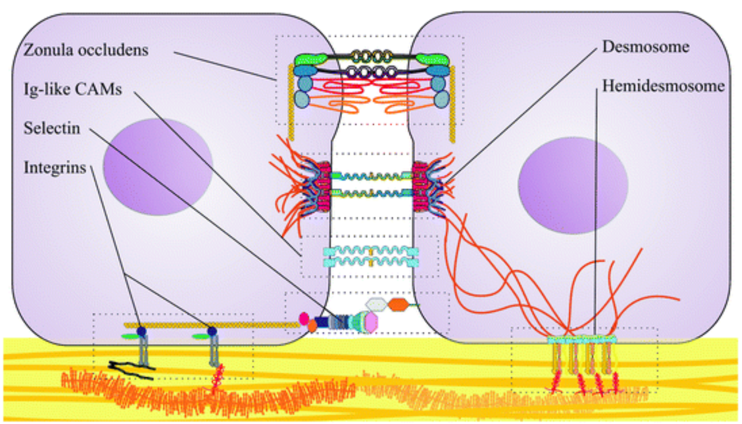
**TABLE 1.1. Some Common Examples of Surface and Colloidal Phenomena in Industry and Nature**

| Surface Phenomena | Colloidal Phenomena |
|---|---|
| *Products Manufactured as Colloids or Surface Active Materials* | |
| Soaps and detergents (surfactants) | Latex paints |
| Emulsifiers and stabilizers (nonsurfactant) | Aerosols |
| | Foods, (ice cream, butter, mayonnaise, etc.) |
| Herbicides and pesticides | Cosmetics and topical ointments |
| Fabric Softeners | Pharmaceuticals |
| | Inks |
| | Lacquers, oil-based paints |
| | Oil and gas additives |
| | Adhesives |
| *Direct Application of Surface and Colloidal Phenomena* | |
| Lubrication | Control of rheological properties |
| Adhesion | Emulsions |
| Foams | Emulsion and dispersion polymerization |
| Wetting and waterproofing | Drilling muds |
| | Electrophoretic deposition |
| *Use for the Purification and/or Improvement of Natural or Synthetic Materials* | |
| Tertiary oil recovery | Mineral ore separation by flotation |
| Sugar refining | Grinding and communition |
| Sintering | Sewage and wastewater treatment |
| *Physiological Applications* | |
| Respiration | Blood transport |
| Joint lubrication | Emulsification of nutrients |
| Capillary phenomena in liquid transport | Enzymes |
| Arteriosclerosis | Cell membranes |

Biocompatibility




Cell adhesion



# Outline

**I: Introduction**
II: Wetting/Dewetting Contact Angle
III: Characterization of Surfaces

Bulk - Interfaces

Surface free energy

Cohesion and Adhesion

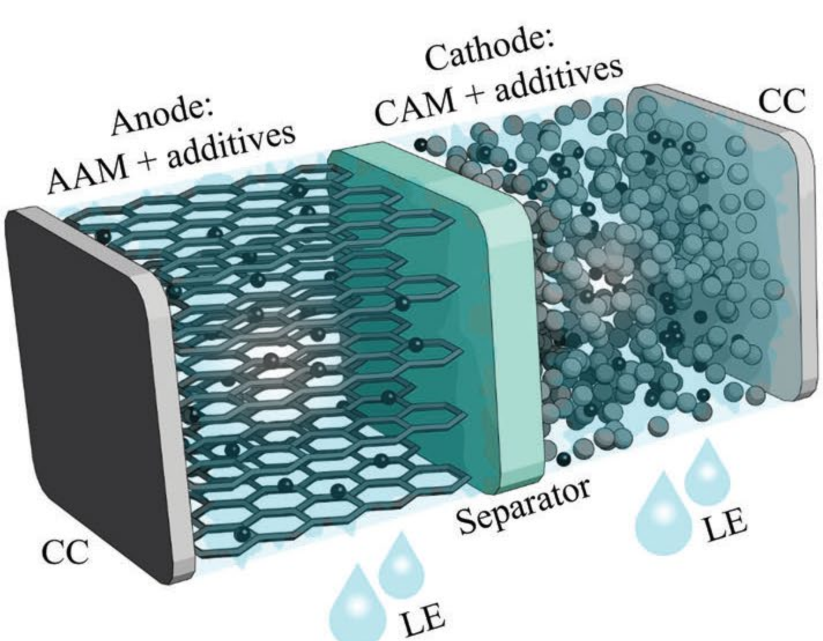
Intermolecular Forces

J. Israelachvili, Intermolecular & Surface Forces, 2nd Edition, **1992**

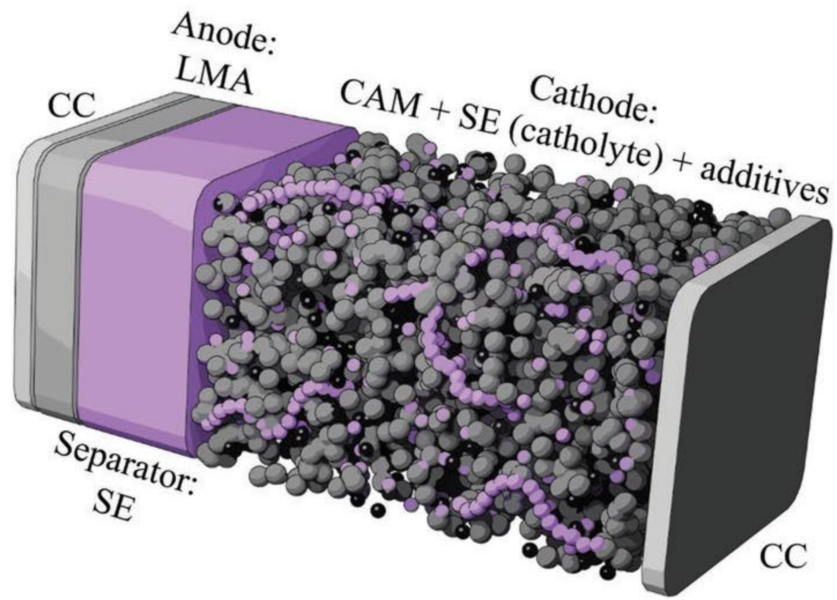
# Bulk – Interface: example Batterie

Graphic representation of

**a classic lithium-ion battery with liquid electrolyte**




**a solid-state battery with lithium metal anode**

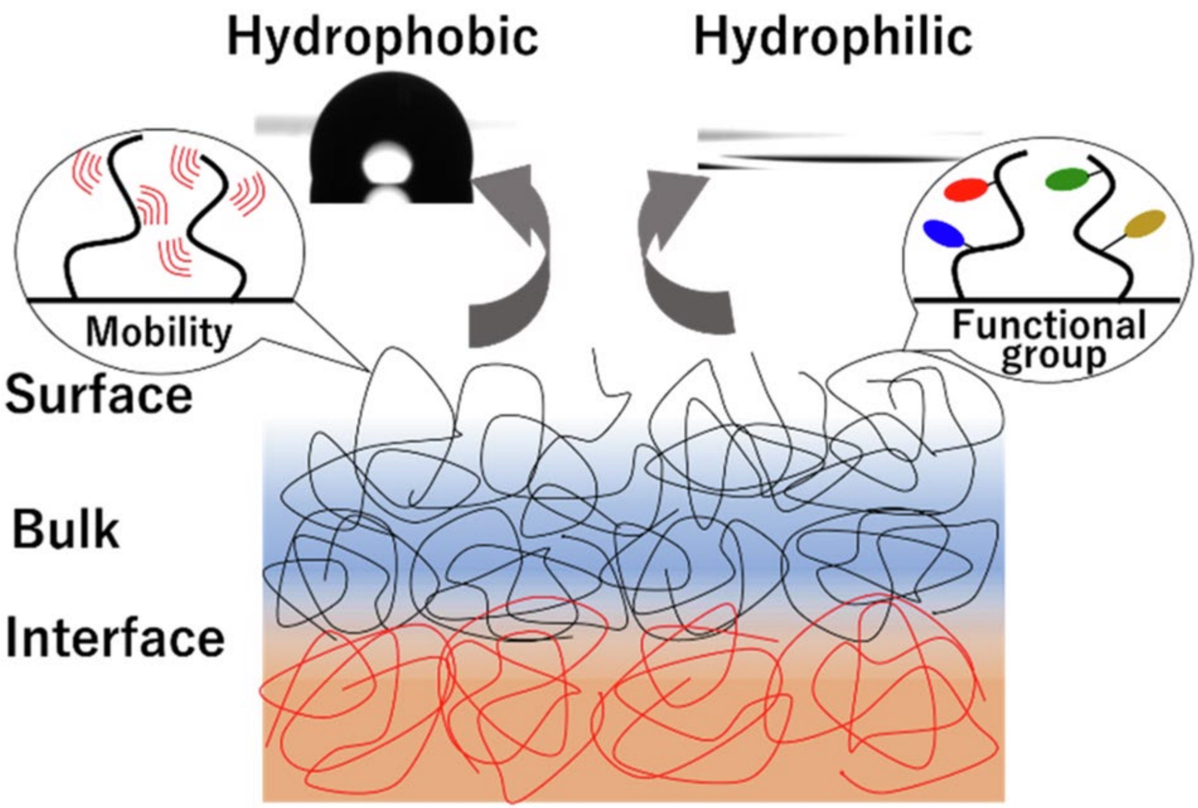



CC: current collector; LE: liquid electrolyte, SE: solid electrolyte;
AAM/CAM: active anode or cathode material; LMA: lithium metal anode

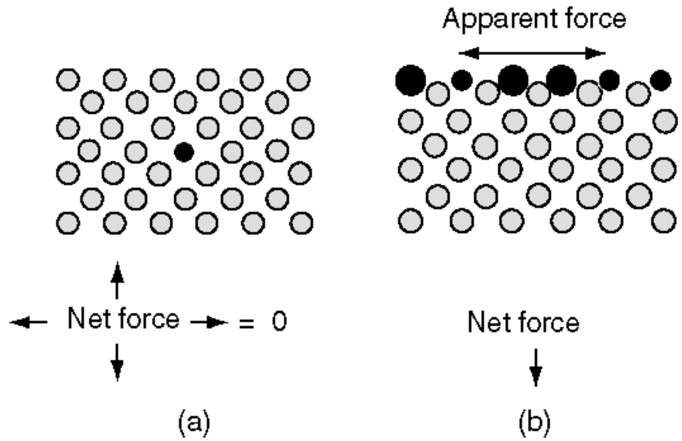
www.isi.fraunhofer.de/de/blog/themen/batterie-update/feststoffbatterien-markt-potenziale-herausforderungen-materialien-komponenten-zellkonzepte.html

# Bulk – Interface - Surface

Surface: Zone of a piece of material where the structure and composition differ from the average (bulk) composition and structure.



# Surface Free Energy

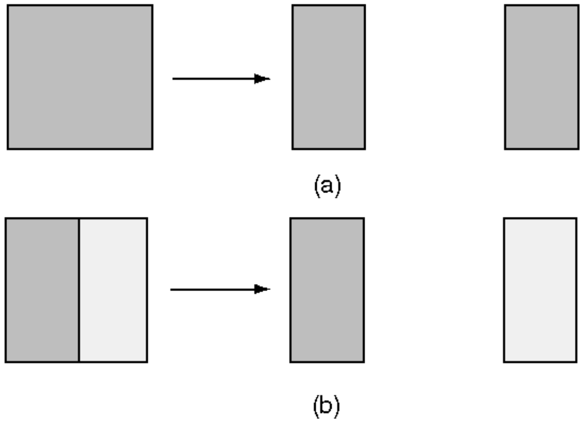



- Atoms or molecules at a surface will experience a net positive inward (i.e., into the bulk phase) attraction normal to the surface, the resultant of which will be a state of lateral tension along the surface; the "**surface tension**".

- The **surface free energy**, or more correctly, the **excess surface free energy** represents the part of the free energy of the system resutling from the units located at the surface.

- **Specific** excess surface free energy = excess surface free energy **per unit area** ($mJ/m^2$)

# Cohesion and Adhesion




**Cohesion**: when new surface is formed by dividing a homogeneous material, a certain amount of work is required. Work of adhesion: $W_c = 2\,\sigma$

**Adhesion**: If the new surface results from the separation of two different materials, the resulting work of adhesion is given by $W_a = \sigma_1 + \sigma_2 - \sigma_{12}$

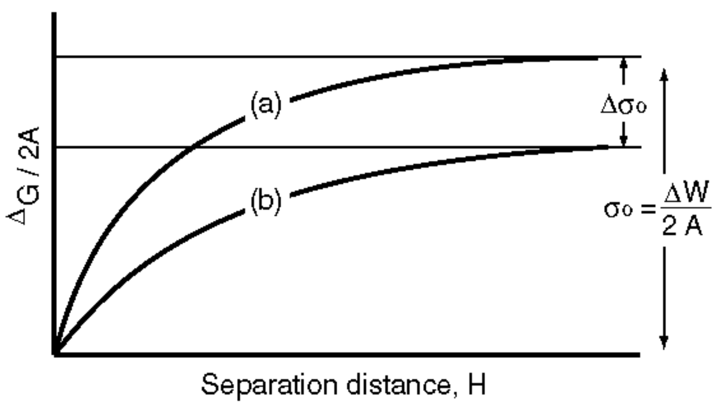



**FIGURE 2.4.** The excess surface free energy of newly formed surface will depend on the nature of the new phase it contacts. (*a*) If the new surface contacts a vacuum, the excess free energy will be maximized. (*b*) If another phase is present (liquid or gas) the excess surface energy will be reduced by an amount depending on the new interactions.

# Forces between Atoms, Ions and Molecules

| Type of interaction | Interaction energy $w(r)$ |
|---|---|
| Covalent, metallic | Complicated, short range |
| Charge–charge | $Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy) |
| Charge–dipole (fixed dipole) | $-Qu\cos\theta/4\pi\varepsilon_0 r^2$ |
| Charge–dipole (freely rotating) | $-Q^2u^2/6(4\pi\varepsilon_0)^2kTr^4$ |
| Dipole–dipole (fixed) | $-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$ |
| Dipole–dipole (freely rotating) | $-u_1^2u_2^2/3(4\pi\varepsilon_0)^2kTr^6$ (Keesom energy) |
| Charge–non-polar | $-Q^2\alpha/2(4\pi\varepsilon_0)^2r^4$ |
| Dipole–non-dipolar (fixed) | $-u^2\alpha(1+3\cos^2\theta)/2(4\pi\varepsilon_0)^2r^6$ |
| Dipole–non-dipolar (rotating) | $-u^2\alpha/(4\pi\varepsilon_0)^2r^6$ (Debye energy) |
| Two non-polar molecules | $-\frac{3}{4}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2r^6}$ (London dispersion energy) |
| Hydrogen bond | Complicated, short range, energy roughly proportional to $-1/r^2$ |

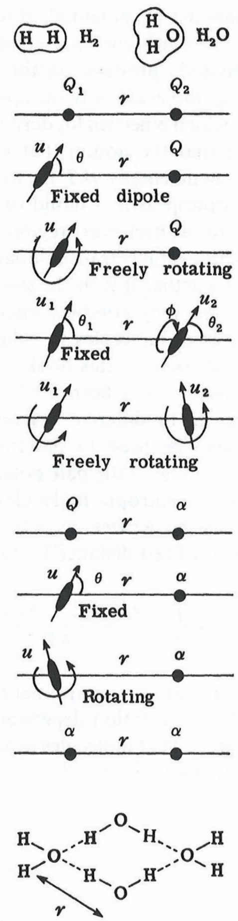
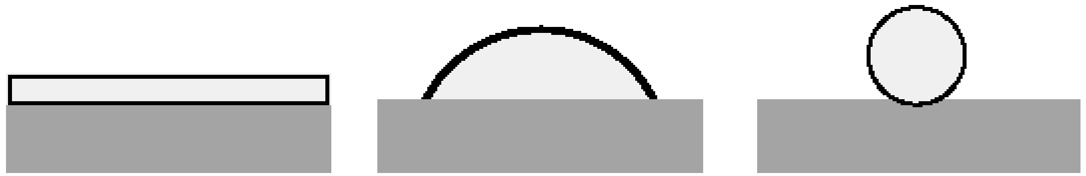



**Fig. 2.2.** Common types of interactions between atoms, ions and molecules in vacuum. $w(r)$ is the interaction free energy (in J); $Q$, electric charge (C); $u$, electric dipole moment (C m); $\alpha$, electric polarizability ($C^2\,m^2\,J^{-1}$); $r$, distance between interacting atoms or molecules (m); $k$, Boltzmann constant ($1.381\times10^{-23}$ J K$^{-1}$); $T$, absolute temperature (K); $h$, Planck's constant ($6.626\times10^{-34}$ J s); $\nu$, electronic absorption (ionization) frequency (s$^{-1}$); $\varepsilon_0$, dielectric permittivity of free space ($8.854\times10^{-12}\,C^2\,J^{-1}\,m^{-1}$). The force is obtained by differentiating the energy $w(r)$ with respect to distance $r$.

# Wetting Behaviour – A Qualitative Look



complete wetting
(uniform film)
$\theta = 0°$

liquid forms convex lens
$0° > \theta > 90°$

complete dewetting
$\theta > 90°$

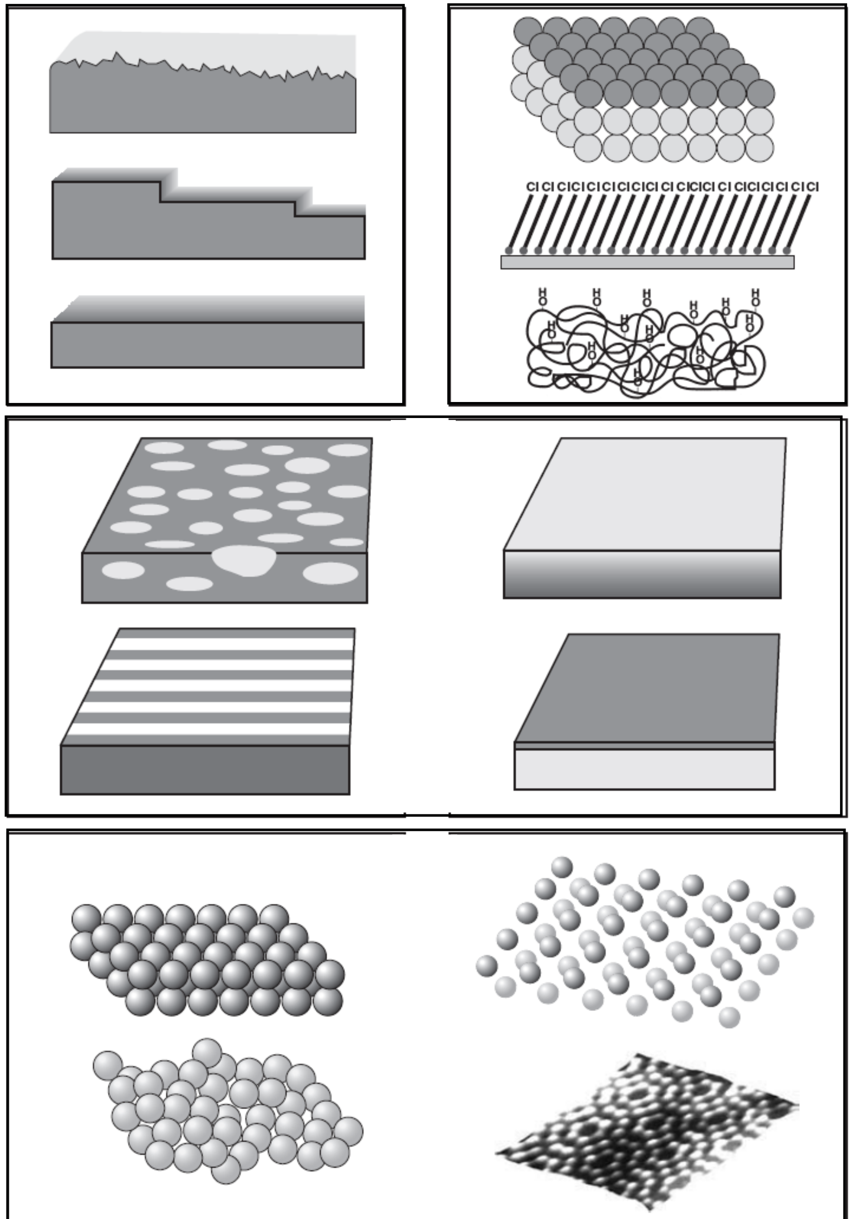
The phenomenon of the **contact angle** can be explained as a balance between the force with which the molecules of the liquid (in the drop) are being attracted to each other(a cohesive force) and the attraction of the liquid molecules for the molecules that make up the surface (an adhesive force).

# Parameters for Surface Characterization

**Topography**

**Surface chemistry**

**Compositional heterogeneities**



**Crystalline vs. amorphous surfaces**

Ch. 1, Buddy D. Ratner, A. S. Hoffman, Frederick J. Schoen, J. E. Lemonds, Biomaterials Science, 2nd edition (Wiley)

# Overview of Surface Characterization Techniques

**TABLE 1** Common Methods to Characterize Biomaterial Surfaces

| Method | Principle | Depth analyzed | Spatial resolution | Analytical sensitivity | Cost[c] |
|---|---|---|---|---|---|
| Contact angles | Liquid wetting of surfaces is used to estimate the energy of surfaces | 3–20 Å | 1 mm | Low or high depending on the chemistry | $ |
| ESCA (XPS) | X-rays induce the emission of electrons of characteristic energy | 10–250 Å | 10–150 μm | 0.1 at% | $$$ |
| Auger electron spectroscopy[a] | A focused electron beam stimulates the emission of Auger electrons | 50–100 Å | 100 Å | 0.1 atom% | $$$ |
| SIMS | Ion bombardment sputters secondary ions from the surface | 10 Å–1 μm[b] | 100 Å | Very high | $$$ |
| FTIR-ATR | IR radiation is adsorbed and excites molecular vibrations | 1–5 μm | 10 μm | 1 mol% | $$ |
| STM | Measurement of the quantum tunneling current between a metal tip and a conductive surface | 5 Å | 1 Å | Single atoms | $$ |
| SEM | Secondary electron emission induced by a focused electron beam is spatially imaged | 5 Å | 40 Å, typically | High, but not quantitative | $$ |

[a] Auger electron spectroscopy is damaging to organic materials and is best used for inorganics.
[b] Static SIMS ≈ 10 Å, dynamic SIMS to 1 μm
[c] $, up to $5000; $$, $5000–$100,000; $$$, >$100,000.