

Cheatsheet Microrobotics

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Scaling

Scaling

- $L^4 \sim$ magnetic force between current carrying wires
 - $L^3 \sim$ mass, volume, heat generation, gravity, force of a magnet on a current carrying wire, torque between two magnets, electromagnetic force
 - $L^2 \sim$ surface, heat loss, Van der Waals force, electrostatic force, force between two magnets
 - $L^1 \sim$ length, surface tension
- Power scales with volume (bad for microscales)

Frequency

Resonant Frequency:
 $f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\frac{g}{l}}$

Frequency Scaling of Cantilever Beam:
 If all dim scaled $\rightarrow L^{-1}$
 If only length scaled $\rightarrow L^{-2}$

Electrostatics

Electric Potential: $Q = \frac{U}{4\pi\epsilon_0 r}$

Electric Field:
 Line Charge: $E = \frac{\lambda}{2\pi\epsilon_0 r}$
 Sheet Charge: $E = \frac{\sigma}{2\epsilon_0}$

- Fundamental Force
- Long-range interactions
- easy to be induced by ionization or polarization
- Major function and failure mechanism of MEMS devices

Capacitance

Formula:
 $E = \frac{U}{d} \rightarrow U = \frac{Q}{C} = \frac{d}{\epsilon_0} \frac{Q}{A} \rightarrow C = \frac{Q}{U} = \frac{\epsilon_0 A}{d}$

Electric Energy:
 $W_T = \frac{U^2}{2} \epsilon_0 \frac{lw}{d}$, where l and w are the length and width of the two plates respectively and d is the distance between them. (differentiate w.r.t. l, w or d to get the force in this direction)

Gripping Strategies

Surface Roughness \rightarrow Van der Waals
 Surface Tension \rightarrow Fluidic Film
 Electrostatic Adhesion \rightarrow Electric Voltage

Magnetism

Magnetism

- The origin of magnetism lies in the atomic and molecular structure of the material. It originated in the atomic structure, such that unpaired electrons in atoms cause a magnetic field due to their movement.
- B (magnetic flux density) is a measure of how a material reacts to an applied magnetic field $H \rightarrow$ via tensor μ which is anisotropic (magnetisation in the magnet is aligned in a certain direction) and non linear.
- Saturation: measure of amount of magnetic field a material can intensify
- Permeability μ : factor of intensification
- There is a H_{sat} where further magnetization is not possible and thus permeability is nonlinear $\mu = dB/dH$ for higher H values.
- Magnetic flux lines are smooth curves, proportional to strength of field, always travel in loops, do not have a source or a sink, can travel through vacuum, follow path of greatest permanence, do not travel through an iron box

H does not depend on the medium, whereas B does. B is the number of magnetic flux lines cutting through a perpendicular plane of given area.

Magnetic Permeability

$$B = \mu H = \mu_0 \mu_r H$$

Magnetization / Magnetic Susceptibility

$$B = \mu_0 H + \mu_0 M = \mu_0 H(1 + \chi)$$

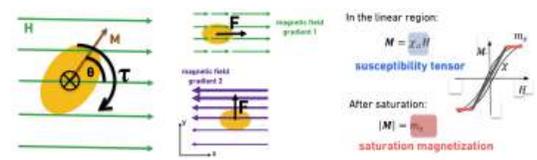
- Magnetization explains: $H = 0 \rightarrow$ remanence, $H \neq 0 \rightarrow$ coercivity
- Soft magnetic materials $H_c < 1000$: $B = (\chi + \mu_0)H \rightarrow$ magnetized with $M = \chi H$ and will stay magnetized
- Hard magnetic materials $H_c > 10000$: $B = \mu_0 H + B_r \rightarrow$ magnetized with M independent from H and will demagnetize
- After saturation ($M = M_{max}$) B will increase with μ (as if vacuum)

8 magnetic Axioms

1. Flux follows path of least resistance (lowest reluctance or highest permanence)
2. Parallel flux lines repel each other if direction is the same
3. Flux lines can never cross
4. Flux always travels in curved or straight lines (never perpendicular)
5. Unsaturated materials have flux lines that leave in normal direction
6. There is a saturation level H_{sat} , where no more flux is possible
7. Flux always travels from north pole to nearest south

pole in closed loops
 8. No monopoles!

Magnetic Force and Torque



In the linear region:
 $M = \chi_v H$
 susceptibility tensor

After saturation:
 $|M| = M_s$
 saturation magnetization

$$F_M = \mu_0 v (M \cdot \nabla) H = \mu_0 v [M \cdot \frac{\partial H}{\partial x}, M \cdot \frac{\partial H}{\partial y}, M \cdot \frac{\partial H}{\partial z}]$$

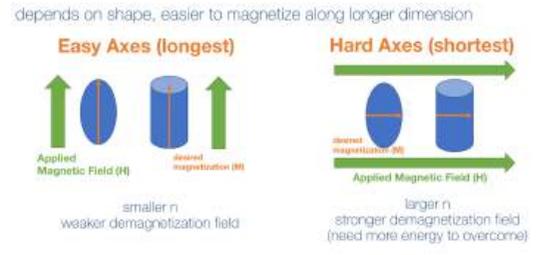
$$\tau_M = \mu_0 v (M \times H)$$

$$m = v \cdot M$$

Where:
 M is the Magnetization field (vector)
 H is the magnetic field (vector)
 μ_0 is the permeability constant
 v is the **Volume of the body!**
 m = magnetic moment

For calculations:
 $a \times b = a \cdot b \cdot \cos(\eta)$
 $a \cdot b = a \cdot b \cdot \sin(\eta)$

Easy Axis and Hard Axis, Demagnetizing Field

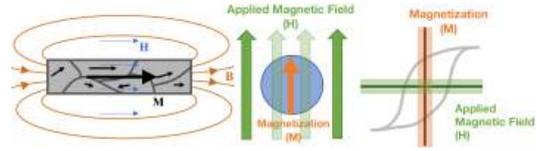


depends on shape, easier to magnetize along longer dimension

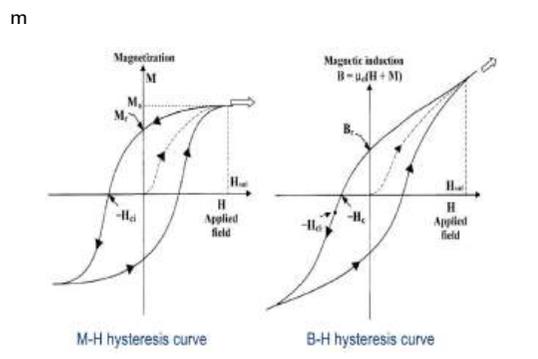
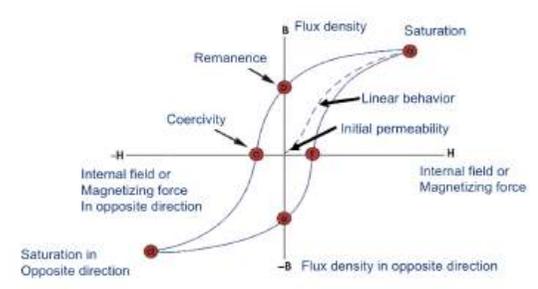
Long axis \rightarrow weak demag. field \rightarrow easy axis
 Short axis \rightarrow strong demag. field \rightarrow hard axis (requires more energy)

$H_{demag.} = -NM$, N is the demagnetizing tensor (depends on shape), M depends on μ ($M = \chi H$) $\mu = \mu_0(1 + \chi)$ $\chi = \frac{\mu}{\mu_0} - 1$

Hysteresis Loop



The magnetization process is conveniently presented in (equivalent) B-H or M-H diagrams



Coercivity is the negative magnetic field required to demagnetize the material ($B=0$). Strong permanent magnets need a high remanence. For memory storage or if you want to, the material should have high coercivity (stability) and high remanence.

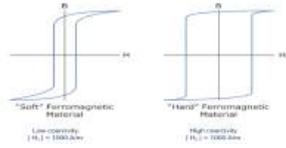
For precise field control
 The electromagnet core should have low remanence, coercivity, permeability and high saturation and the microrobot should have high remanence and coercivity. The slope of the B-H curve is the permeability.

Controlling Movement for microrobots
 The material with the highest remanence and the highest coercivity. In order to precisely manipulate the microrobot, its magnetic moment should be stable (high coercivity) to apply torque for rotations and its magnetic moment should be as big as possible (high remanence) to apply large forces for translations.

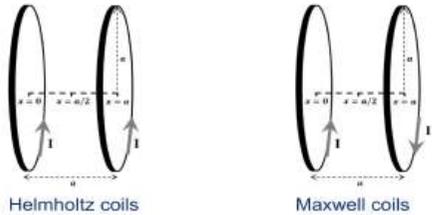
Soft Magnetic vs Hard Magnetic Materials

Hysteresis loop: **Hard magnetic** \rightarrow high remanence, M is independent, once magnetized. **soft magnetic** \rightarrow (almost) no remanence
 Soft magnetic materials cannot be permanently magnetized:

- Magnetization directly depends on H field and on shape (susceptibility factor) $M = \chi H$
- Force does not depend on field gradient only but also indirectly on H



Helmholtz and Maxwell Coils



a = radius of coils = distance between coils
Helmholtz Coil (current flow in same direction):
 Field along central axis:

$$|H| = \left(\frac{Ni}{2a}\right) \left[\left(1 + \frac{x^2}{a^2}\right)^{1.5} + \left(1 + \frac{(a-x)^2}{a^2}\right)^{1.5} \right]$$

Uniform magnetic field (zero gradient) between coils
Maxwell Coil (current flow in opposite direction):
 Field along central axis:

$$|H| = \left(\frac{Ni}{2a}\right) \left[\left(1 + \frac{x^2}{a^2}\right)^{-1.5} - \left(1 + \frac{(a-x)^2}{a^2}\right)^{-1.5} \right]$$

Uniform field gradient and zero field between coils
 In combination it's possible to manipulate the field and the gradient (change in the field) independently from each other

Electromagnets

Field along axis of a solenoid:

$$|H| = \left(\frac{Ni}{L}\right) \left[\frac{L+2x}{2[D^2+(L+2x)^2]^{1/2}} + \frac{L-2x}{2[D^2+(L-2x)^2]^{1/2}} \right]$$

At the center of the axis:

$$|H| = \left(\frac{Ni}{L}\right) \left[\frac{L}{(L^2+D^2)^{1/2}} \right]$$

For long solenoids ($L \gg D$):

$$|H| = \frac{Ni}{L}$$

The field of the solenoid at the end is half of the field in the center.

Motion in Liquids

Reynolds Number

$$Re = \frac{\rho u L}{\mu}$$

$\rho u L$ = Inertial effects
 μ = Viscous effects
 L and u small in microrobotics

Navier Stokes Equation

General equation (and valid for **intermediate flow 1 « Re » 10'000**)

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p + \mu \nabla^2 \mathbf{u}$$

Non-dimensionalized Navier-Stokes Equation:

$$\frac{\rho v_c L}{\mu} \left(\frac{\partial \tilde{\mathbf{v}}}{\partial \tilde{t}} + (\tilde{\mathbf{v}} \cdot \tilde{\nabla}) \tilde{\mathbf{v}} \right) = -\tilde{\nabla} \tilde{p} + \tilde{\nabla}^2 \tilde{\mathbf{v}}$$

$\tilde{\mathbf{v}} = \frac{\mathbf{v}}{v_c}$, $\tilde{t} = \frac{t v_c}{L}$, $\tilde{p} = \frac{pL}{\mu v_c}$
 v_c : characteristic velocity
 L : characteristic length
 μ : viscosity

High Reynold Number / Re » 10'000 (Turbulent Flow)

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = -\nabla p$$

→ viscous effects ≈ 0

Low Reynold Number / Re « 1 (Stokes Flow)

$$\nabla p = \mu \nabla^2 \mathbf{u}$$

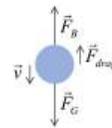
→ inertial term ≈ 0

Stokes Flow is Time-Independent. That means the pattern of motion is the same, whether slow or fast, whether forward or backward in time. Stokes flow will creep around structure.

Stokes Drag and Rotational Drag

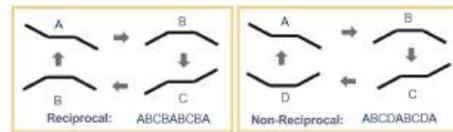
$$F_{drag} = 6\pi\mu R u$$

$$\tau_{drag} = 8\pi R^3 \mu \omega$$



Implication

- You can't move forward with only **Reciprocal Movement**
- You need **Non-Reciprocal Movement** (like corkscrew motion) to move in a low Reynolds number environment.



Diffusion in Liquids

Viscosity of Liquids

$$\mu = \frac{\tau}{\dot{\gamma}}$$

μ : Viscosity
 τ : Shear Stress
 $\dot{\gamma}$: Shear Rate

Newtonian Fluids: Constant Viscosity
 Shear Thickening: Higher Viscosity, higher Shear Rate
 Shear Thinning: Smaller Viscosity, smaller Shear Rate

Viscoelasticity: viscous + elastic (time-dependent)

Relaxation: stress decrease in constant strain
 Creep: strain increases in constant stress

Brownian Motion

D : Diffusivity
 k : Boltzmann's Constant
 T : Temperature
 R : Radius
 μ : Viscosity

$$D = \frac{kT}{6\pi R \mu}$$

Mean squared displacement:

- 1D: $\langle r^2 \rangle = 2Dt$
- 2D: $\langle r^2 \rangle = 4Dt$
- 3D: $\langle r^2 \rangle = 6Dt$

Random Walks

Non-Biased/Biased

Biased

Thermophoresis: particle experiences force towards lower temperature.

Electrophoresis: charged particle experiences force due to potential difference in environment.

Dielectrophoresis: mismatch in polarization between medium and particle causes an "effective dipole", thus a force.

Formula

Hage-Poiseuille equation

For laminar, stationary, newtonian flows

$$Q = \frac{\pi r^4 \Delta p}{8\mu L}$$

Q = Volumetric flow, L = length, Δp = Pressure drop, r = radius

Propulsion Matrix



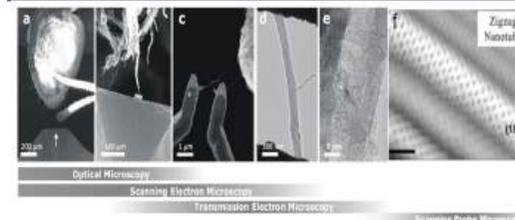
$$\begin{pmatrix} F \\ \tau \end{pmatrix} = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \cdot \begin{pmatrix} u \\ \omega \end{pmatrix}$$

The forward velocity and the rotational velocity are coupled!

Oscillating magnetic field $\mathbf{H}(t)$ around y axis:

$$\mathbf{H}(t) = \begin{pmatrix} \cos(\omega t) \\ 0 \\ \sin(\omega t) \end{pmatrix}$$

Observation Tools



Optical Microscopy

Magnification

- Scanning lens (4x)
- Low power lens (10x)
- High power lens (40x)
- Immersion lens (100x)

Overall magnification is given as the product of the objective lens and ocular lens (1000x magnification possible):

$$M = M_1 \cdot M_2$$

The Nature of Light

- Snell's law for reflection and refraction:

$$\frac{\sin(\theta_1)}{\sin(\theta_2)} = \frac{n_2}{n_1}$$

Diffraction Light rays bend around edges - new wavefronts are generated at sharp edges

The smaller the aperture the bigger the diffraction

Dispersion Separation of light into its constituent wavelength when entering a optical medium

Resolution

Theoretical optical resolution is the finest of detail that can be distinguished:

$$d = \frac{0.61\lambda}{n \cdot \sin\alpha} = \frac{0.61\lambda}{NA}$$

d : minimum resolving distance

λ : wavelength of the light being used

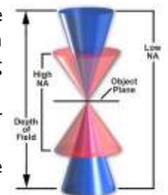
n : index of refraction of embedding medium

α : acceptance angle of the objective lens

Numerical aperture: $NA = n \cdot \sin\alpha$
 measure of light gathering capabilities of a lens

Highest practical numerical aperture 1.5 (with oil)
 Best optical resolution: 200 nm

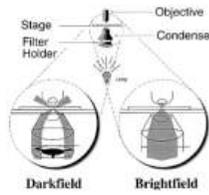
Depth of Field (DOF) is the range of distance along the axis in which the sample can move without losing the sharpness of the image. The higher the NA, the shallower the DOF. The higher the magnification, the lower the DOF.



Contrast

- Bright Field: Full aperture illuminated, low contrast, light absorption of sample is imaged

- **Dark Field:** central obstruction blocks the central light cone, enhances contrast by indirect illumination, light scattering at sample is imaged



Aberration

- **Spherical Aberration:** Light waves passing through edge of uncorrected convex lens not in focus with those passing through center
- **Chromatic Aberration:** Optical lens has different refractive indices for different wavelengths
- **Astigmatism:** Optical system is not axis-symmetric, or error in shape

Applications: Everyday lab use, observe samples directly without altering them, determine protein concentrations in living cells using UV-fluorescence imaging, image samples where no resolution lower than 200 nm is needed.

Limitations: Resolution limited by diffraction. The resolution limit is a function of the wavelength of light. Theoretical optical resolution: $d = 0.61 \lambda / N.A.$ Transparent samples or different samples with similar transparencies are difficult to image.

Electron Microscopy

Nature of electrons

$$\lambda = \frac{h}{mv}, eV = \frac{1}{2}mv^2$$

Electrons are charged particles. They can be accelerated in an electrostatic field. The trajectory of an accelerated charged particle can be deflected by electrostatic and/or magnetic fields. For example with Lorenz Law: $F = q(v \times B)$

Theoretical resolution of electron microscopy

$d = 0.6\lambda_e$, Real resolution of electron microscopes under 300 kV is around 0.2 nm (aberrations)

SEM, Scanning Electron Microscopy

Electron gun emits electron, Beam is focused on condenser lenses, Scan coils are used to move the focus spot, Detection of back-scattered electrons and secondary electrons, Creation of each pixel on image based of number of electrons.

High-angle secondary electron (SE) detector

- SE are electrons emitted from the top layer
- Sample surface (topography)
- Low acceleration voltage (1kV-5kV)

Backscatter electrons (BSE) detector

- BSE are from deeper layer of the sample
- material contrast
- Low acceleration voltage (3kV-5kV)

In-lens detector (low-angle secondary electrons)

- SE generated by low energy primary beam (-20keV)
- Sample surface, edge structure
- Low acceleration voltage (0.1kV-3kV)

Resolution: 1-20 nm (lower resolution than TEM)

Applications: Image microstructures, surface topography, material compositions.

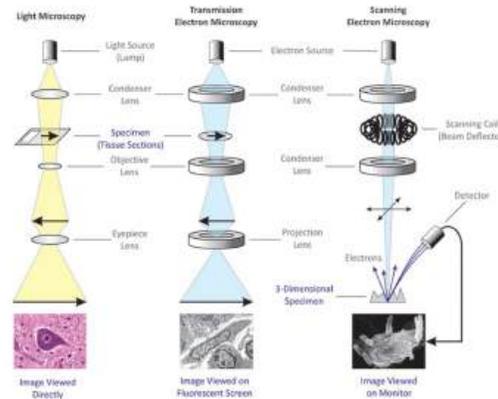
Limitation: The samples must be solid. It is not possible to observe wet samples and living cells. Often a high vacuum and a conducting coating is needed, which both can alter the sample. Due to electron scattering, the electrons from the electron beam interacts with a larger area than just on the focused spot. This limits the resolution.

TEM, Transmission Electron Microscopy

Image view on fluorescent screen. Electrons go through sample. Atomic level resolution. **Imaging mode:** Bright field/ dark field imaging **Diffraction mode:** The periodic structure of a crystalline solid acts as a diffraction grating, scattering the electrons in a predictable manner. Reproducing the structure of the crystal from the observed diffraction may be possible.(e.g protein crystal)

Applications: Observing thin samples (e.g. thin slices of brain tissue), crystallography (atomic arrangement).

Limitations: Limitations: Long sample preparation time. A thin sample is needed. Sample preparation can alter the sample. Resolution limited by electron diffraction. Higher acceleration voltage (smaller wavelength) increases the resolution, but simultaneously increases the damage introduced in the sample. High vacuum is needed.



SPM, AFM

Scanning Probe Microscopy (SPM)

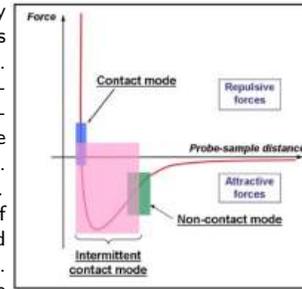
Techniques using a scanning probe to study probe-surface interactions

Atomic force Microscopy (AFM)

Atomic resolution, sub-nanometer!

Contact mode:

By scanning a tip across the sample surface. Monitoring the cantilever change with a laser diode. Force range = $[0.01N/m, 1N/m]$. In ambient and liquid. Static deflection of cantilever is used to calculate force. Measurement is prone to noise and drift, low-stiffness cantilevers → boost deflection signal.



⊕: High scan speeds (throughout) Rough samples with extreme changes in vertical topography can sometimes be scanned more easily in contact mode. ⊖: Lateral (shear forces can distort features in the image The combination of lateral forces and high normal forces can result in reduced spatial resolution and may damage soft samples due to scraping between the tip and sample.

Intermittent Contact mode (Tapping): By scanning a tip of an oscillating cantilever across sample surface. Near it resonance frequency [20nm,100nm]. The tip lightly taps on surface. Ambient and liquid. Less force. ⊕: Higher lateral resolution on most samples Lower forces and less damage to soft samples Lateral forces are virtually eliminated, so there is no scraping. ⊖: Slightly slower scan speed than contact mode AFM.

Feedback: The Feedback loop has a constant Amplitude.

Non-contact Mode: Cantilever is oscillated slightly above resonance frequency(10nm). No contact. Cantilever is decreased by Van der Waals forces. For tapping and non-contact higher stiffness to get higher resonance frequencies. Higher frequencies → lower noise levels.

⊕: No force exerted on the sample surface. ⊖: Lower lateral resolution, limited by the tip-sample separation Slower scan speed than Tapping Mode and Contact Mode Non-contact usually only works on extremely hydrophobic samples, where the adsorbed fluid layer is at a minimum.

Feedback: The feedback loop either has constant Amplitude or constant Frequency.

Application: Observing and manipulating nanometer-sized objects, nanolithography, measuring magnetic surface pattern (MFM), measuring biological samples in a wet environment.

Limitations: Slow scanning rate and small scanning area. Sharp edges and overhangs cannot be imaged. The size of the probe tip sets a resolution limit (smallest theoretical tip = one atom). The tip can crush into the sample when large topological heights differences are present. The tip can damage the sample. Friction and adhesion can influence the measurement.

Other observation tools

Magnetic Force Microscopy (MFM)

Uses a tip coated with a magnetic material. Magnetic features are often hidden in topographic image. Lift mode scans magnetism. Tapping mode scans topography.

Near Infra-Red Imaging

Biologically transparent or near Infrared Window (700-1700 nm). The longer wavelength can penetrate some tissue and scatter at more deep tissue. With the reflected light it is possible to build an image.

Magnetic Resonance Imaging (MRI)

Clinical MRI measures the spatial distribution of protons in the body. The gradient field slightly distorts the main magnetic field in a predictable pattern, causing the resonance frequency of protons to vary in as a function of position. **Radio Frequency (RF)** coils are used to send a strong pulse at the Larmor frequency. The decay signal is then measured by another set of RF coils. **Lamor Frequency:** $\omega = \gamma B$, γ is the gyromagnetic ratio.

Magnetic Particle Imaging

Images the spatial distribution of superparamagnetic iron oxide particles (SPIOs). Signal can penetrate tissues virtually unattenuated, allowing the inspection of regions located deep below the surface. Low field-strength compared to MRI and less costly equipment. High spatial resolution (0.4 mm) and high imaging speed (20 ms). MPI requires: ferromagnetic nano-particles, a static magnetic field, an oscillating field (drive field), and signal receive coils.

Working principle: MPI relies on the nonlinearity of the magnetization curves of ferromagnetic material and the fact that the particle magnetization saturates at some magnetic field strength. When exposed to an oscillating magnetic field (drive field), the spectrum of the responding magnetization contains not only the base frequency f but also higher harmonics that are used for imaging.

Positron Emission Tomography (PET)

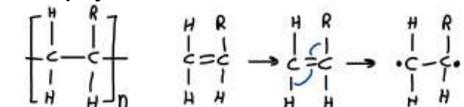
PET is an in-vivo tracking or localization technique.

Materials for Microrobots

Polymers

Polymers are formed from **Monomers** and this process is called **polymerization**. There are different types of polymerization:

Addition polymerization



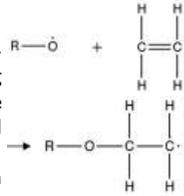
- monomers contain double bonds
- double bond breaks
- new bond with another monomer forms
- General formula: $nA \rightarrow P_n$
- **Initiation:** A radical gets formed by energy input (can be in the form of heat, light, radiation)
- **Propagation:** Radical Monomers react with free

monomers in fast succession. During propagation the formed macromolecules active site continuously relocate at its growing end

- **Termination:** The polymer chains radical site reacts with another free radical

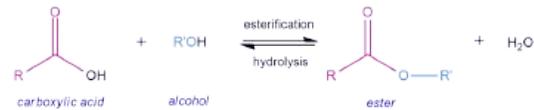
Radical polymerization

- Initiation: Energetically induced molecule bond breaking forms radicals (Radical: a free molecule with an unpaired number of electrons)
- Propagation: Reaction with another monomer forming a new radical
- Termination: Reaction between two radicals



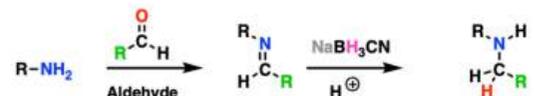
Polyesters (Condensation polymers)

- Esterification: $RCOOH + R'OH \rightarrow RCOOR' + H_2O$
- Monomers A having reactive carboxyl group polymerizing with monomers B having hydroxyl group
- General formula for condensation polymerization: $nA + nB \rightarrow P_n + nH_2O$



Polyamides (Condensation polymers)

- Amination: $RCOOH + H_2NR \rightarrow RCONHR + H_2O$
- General formula for condensation polymerization: $nA + nB \rightarrow P_n + nH_2O$



Radical: double bond breaks. Polyester O / Polyamide N: H_2O as side product.

Polymer crosslinking Bond formation between polymer chains

- Chemical crosslinking: strong bonds between chains, covalent bonding, high strength and durability
- Physical crosslinking: weaker interactions between chains, ionic or weaker interactions, low strength and durability

Hydrogels: Water insoluble 3D network interconnected polymers. Hydrophilic or amphiphilic molecules. At least 10 percent water. Water absorption is dependent on: pH, Ionic conditions, temperature etc. Easy incorporation and release of drugs. Volume/mass Swelling ratio: $Q = \frac{V_s - V_d}{V_d}, q = \frac{m_s - m_d}{m_d}$

Magnetic Material

Origin → spin of electrons and electron orbital motion

- Diamagnetic: fully paired electrons
- Paramagnetic: unpaired electrons

Magnetism requires interactions between neighbouring magnetic atoms. Atomic arrangements with respect to each other play a key role. Exchange interactions occurring between neighbouring atoms determine the displayed magnetic behaviour. That's why Fe, Co and Ni are more magnetic than Mn or Gd.

Temperature-dependent Hysteresis

Ferromagnetic material displays paramagnetic behavior above Curie-Temperature
Ferromagnetic behavior of superparamagnetic objects if cooled below their blocking temperature.

X-ray crystallography By analysing the x-ray diffraction pattern it's possible to determine the three dimensional crystal structure.

Magnetic materials for biomedical applications

- Ni & Co toxic, Fe biocompatible but depends on application area
- bcc Fe highly magnetic ($M_s \sim 200$ emu/g) but synthesis extremely challenging
- Fe tends to oxidize (faster at smaller scale)

Iron Oxides

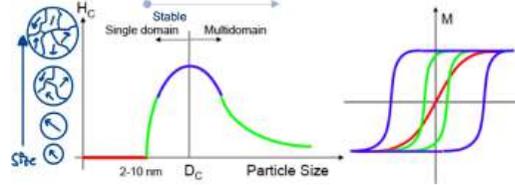
Fe cations ionically bonded to O anions building a crystal structure

- **Wustite** Fe_xO ($x=0.83-0.96$) → antiferromagnetic, Structure: cubic, Spin configuration: anti-parallel
- **Magnetite** Fe_3O_4 → ferromagnetic ~92-100 emu/g
- **Maghemite** $\gamma - Fe_2O_3$ → ferromagnetic ~70-80 emu/g, occurs in 4 different crystal structures each with their own magnetic properties, Structure: Inverse spinel, Spinconfiguration: Mixed parallel/ antiparallel
- **Hematite** $\alpha - Fe_2O_3$ → antiferromagnetic ~0.3 emu/g

<p>Wustite:</p> <ul style="list-style-type: none"> • $Fe(II)_xO$ ($x = 0.83-0.96$) • Rock-salt structure • Antiferromagnetic 	<p>Magnetite:</p> <ul style="list-style-type: none"> • $[Fe(III)]_1 [Fe(II)Fe(III)]_2 O_4$ • Inverse spinel structure • Ferrimagnetic (~92-100 emu/g)
<p>Maghemite:</p> <ul style="list-style-type: none"> • $[Fe(III)]_1 [Fe(III)_{0.5}Fe(II)_{0.5}]_2 O_4$ • Inverse spinel structure • Ferrimagnetic ($M_s \sim 70-80$ emu/g) 	<p>Hematite:</p> <ul style="list-style-type: none"> • $Fe(III)_2 O_3$ • rhombohedral, corundum structure • Antiferromagnetic/ weak Ferrimagnetic

Size dependent magnetism

- if size decreases beyond critical diameter D_c a multidomain structure becomes energetically unfavorable. D_c depends on the materials anisotropy K .
- $\frac{\text{surface}}{\text{volume}}$ increases → surface related spin distortions dominate magnetic behaviour



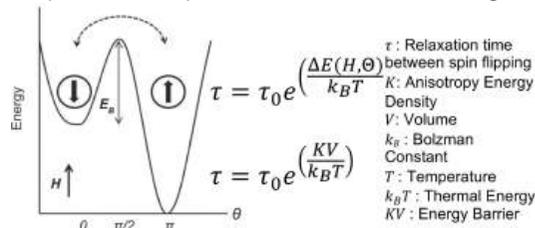
Superparamagnetism

If size decreases further the anisotropic energy decreases, leading to a decreasing energy barrier between magnetic stable states. The object starts to display superparamagnetic behaviour.

Superparamagnetism is related to spontaneous occurring random spin flips between the objects magnetic stable states. The object is characterized by zero coercivity and remanence.

Supermagnetism describes the effect of random flips of the magnetization direction in small ferro and ferri magnetic particles under influence of temperature. According to the Stoner Wohlfahrt Model the energy barrier (E_b) between its magnetic stable states is directly dependent on its anisotropic energy → E_b decreases proportionally with decreasing particle size. Below a certain diameter D_S the thermal energy provided by the surrounding is large enough to overcome the energy barrier. Spontaneous spin flips occur randomly with a frequency defined by the object's Neel relaxation time: τ

If temperature decreases below the specific blocking temperature TB, particles behave like a ferromagnet.



Paramagnetism vs Superparamagnetism

Paramagnetism: Paramagnetic materials have a magnetic susceptibility only in the presence of an external magnetic field. Ferromagnetic materials (i.e. materials experiencing a long-range ordering phenomenon causing to form aligned regions called Weiss domains and can display remanence even after the external field is removed) become paramagnetic when they are heated beyond their Curie temperature. The heating randomizes the magnetic orientation and removes any remanence. Paramagnetism is found in paramagnetic materials and in ferromagnetic materials at temperatures beyond their Curie temperature

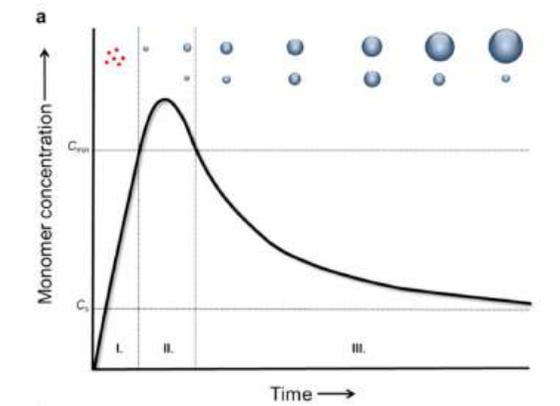
Superparamagnetism: The material in its bulk form is ferromagnetic. Each particle will be a magnetic domain, and will have no remanence, i.e. it behaves like a paramagnetic material but below its Curie temperature. Superparamagnetism is found in a ferromagnetic material

below its Curie temperature as the size is reduced to a few nanometers

Supermagnetism at very small sizes

Nanoparticle's magnetic behaviour is determined by its underlying atomic spin structure. If below 7nm the particles surface to volume ratio starts to drastically increase: Surface related effects such as spin canting start to dominate the particle magnetic behaviour. Spin-canting (Spinneigung), layer of unordered spins, starts to dominate the particles magnetic behaviour.

La Mer Process

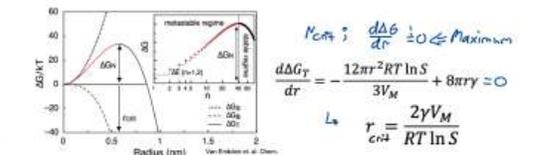


Stage I: Monomer production and accumulation. Monomers are formed from reagents, but commonly thermodynamically unstable by themselves. As a reaction time increases monomer concentration $[M]$ increases until reaching a critical value $[M]_c$

Stage II: Particle Nucleation. The formed crystals total free energy is dependent on its bulk contribution and surface contribution. Free energy change according to La Mer:

$\Delta G_T = \Delta G_B + \Delta G_S$
Nanoparticle have huge A/V ratios → the interfacial energy (Grenzflächenenergie) dominates at very small scale. Free Energy per unit volume: $\Delta G_V = -\frac{RT}{V_M} \ln S$

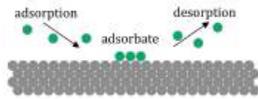
Bulk free energy: $\Delta G_B = \frac{4\pi r^3}{3} \Delta G_V$
Surface free energy: $\Delta G_S = 4\pi r^2 \gamma$
⇒ Free energy change:
 $\Delta G_T = \frac{-4\pi r^3 RT \ln(S)}{3V_M} + 4\pi r^2 \gamma$, where γ is the surface energy and V_M is the molar volume of the monomer.



Stage III: Particle Growth. After stable nuclei formation crystal growth proceeds with monomer addition on the surface until M reaches M_0

and Ostwald ripening: Small particles ($r < r_{crit}$) dissolve in order to facilitate growth of larger particles.

Surface Modification



Adsorption due to collisions with gas atoms. Impact frequency $n_s = \frac{2.7 \times 10^{22} P}{\sqrt{MT}} \text{ cm}^{-1} \text{ s}^{-1}$

P: Pressure, M: Molecular weight, T: Temperature

Adsorption

Adhesion of molecules or atoms within a gas/liquid to a surface. $\eta = \frac{\text{number of occupied adsorption sites}}{\text{number of adsorption sites present}}$

Physisorption: Due to Van der Waals interactions, non-specific, weak, multi-layer growth possible, $\Delta H_{des} = 20 \frac{\text{kJ}}{\text{mol}}$

Chemisorption: Due to chemical bond between adsorbate and substrate, specific for substrate and anchoring group, strong, maximum coverage is a monolayer, $\Delta H_{des} = 200 \frac{\text{kJ}}{\text{mol}}$, can change electronic characteristic of the surface.

Desorption

Chemical bonds break removing the adsorbed species. It is activated by providing enough energy to adsorbed molecule (E_d). It is temperature dependent.

Polanyi-Wigner equation: $-\frac{dN_i}{dt} = v_i \cdot N_i^m \cdot e^{-\frac{E_{d,i}}{RT}}$

N_i : Surface concentration of the adsorbate, v_i : frequency factor, $E_{d,i}$: desorption activation energy, m : order of the desorption reaction.

Stabilization of nanoparticles in aqueous media

Particles must be stable in a polar environment and should avoid interacting with each other.

Via Steric hindrance: Graft long Hydrophilic Polymer chains (Such as PEG or PVP) onto the particle surface providing them with a Hydrophilic character and steric hindrance (Räumliches Hindernis) between each other.

Via electrostatic interactions: Grafting Molecules terminated with ionic moieties onto the Particles providing the particles with a polar surface and introducing an electrostatic repulsion between each other

Microfabrication

When fabricating microstructures, a **static self assembly is preferred** over a dynamic self assembly.

Static self assembly: System is at free energy minimum, no external energy required.

Dynamic self assembly: System forcefully prevented from reaching free energy minimum, requires constant supply of energy (bunch of fish).

Substrates

Substrate is mostly silicon. The unit cell of Si crystal can

be seen as two overlapping simpler unit cells and has a diamond cubic crystal structure.

Miller indices: $\frac{1}{\text{Axis Intercept}} \cdot \text{LeastCommonMultiple}$, negative numbers written with bar on top ($-1 = \bar{1}$).

Oxidation: Oxidation layer acts as a mask, insulating layer, or sacrificial layer. The oxide consumes silicon to grow. $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$

Lithography

Lithography Process

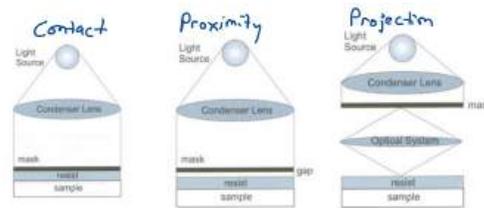
- Clean silicon wafer **spin-coated** with photoresist.
- Photomask: A glass or mylar mask coated with an opaque film defines the features.
- Exposure: A mask aligner is used to pass UV light through the mask onto the wafer.
- Development: Exposed photoresist is washed away, unexposed resist remains.
- Case 1 Additive: Deposition: Metallic or semiconducting layers are evaporated or sputtered onto the surface. Then Lifting-off: Photoresist removed leaving the deposited features.
- Case 2 Subtractive: Wet or Dry etching: Exposed sections are etched away while resist protects the rest. Then Resist Removal: Photoresist is removed leaving etched features.

Exposure

Contact printing: High resolution ($\leq 0.5 \mu\text{m}$), Mask and wafer can be easily damaged.

Proximity printing: 2-4 μm resolution (diffraction effect), 10-25 μm gap (long mask life)

Projection printing: Highest resolution ($\leq 0.2 \mu\text{m}$), Image of mask reduced, Scanning of small field, Complicated and expensive optical setup

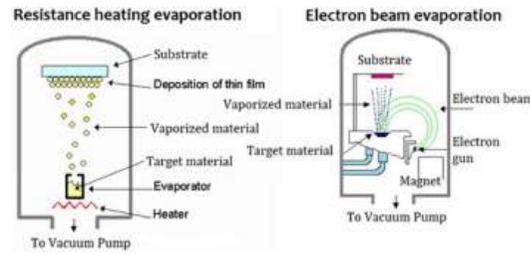


Additive Processes

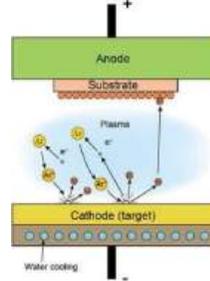
PVD: Physical Vapour Deposition

In thermal, source material is heated until it evaporates. The evaporated material travels to the substrate where it condenses and is deposited.

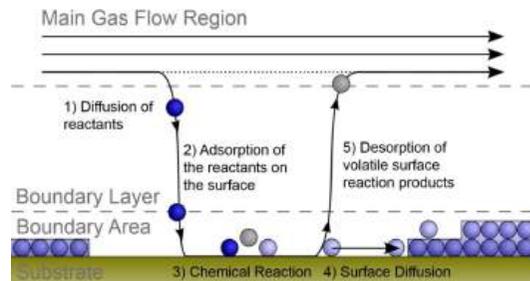
Resistance Heating Evap. - Electron Beam Evap.



Sputtering Argon is ionized by a strong potential difference, these ions are accelerated to a target, after impact the target atoms are released and travel to the substrate, shadowing effect due to the straight trajectory of vapor molecules.



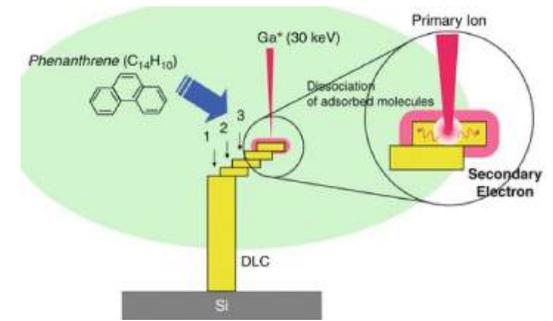
CVD: Chemical Vapour Deposition



Chemical process in gas, Precursor gases react or decompose and precipitate on the substrate to form the coating. Sometimes precursor gases can react with the substrate as well to form a coating. Mostly metal compounds; Si compounds and carbon nanotubes are deposited, Slow, Accurate, Mass transport of the reactant in the bulk (in the gas flow)

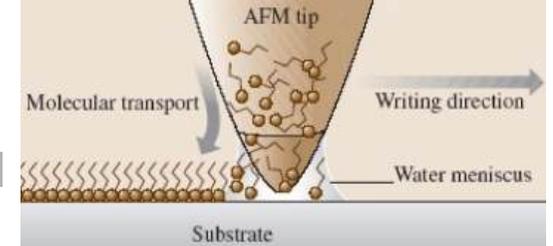
FIB-CVD: Focused Ion Beam Chemical Vapor Deposition

The FIB can be combined with a gas source which delivers reactants to the surface. The adsorbed reactants react with the ion-beam and secondary electrons to form a deposit. Because of the short penetration depth, the deposition area is limited to a small area on the surface. The FIB-CVD is used to fabricate three-dimensional nanostructures.

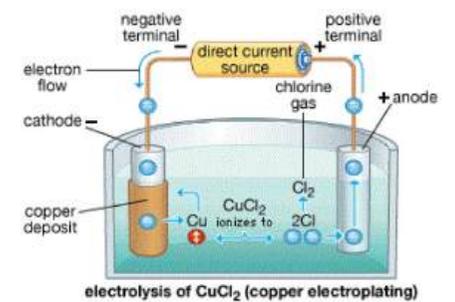


DPN: Dip Pen Nanolithography

the tip of an AFM is inked by dipping the tip in a solution containing a small concentration of the molecules of interest and brought into contact with the surface. The water meniscus that naturally forms between the tip and the surface enables the diffusion and transport of the molecules.



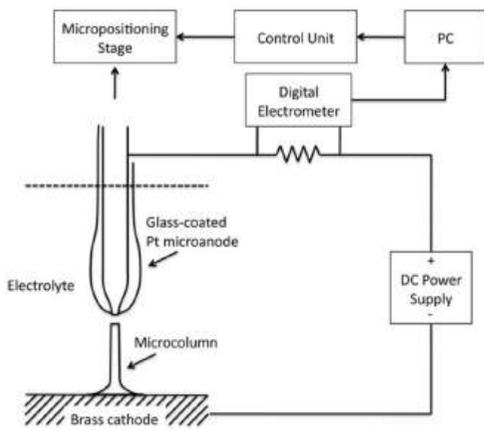
Electrodeposition



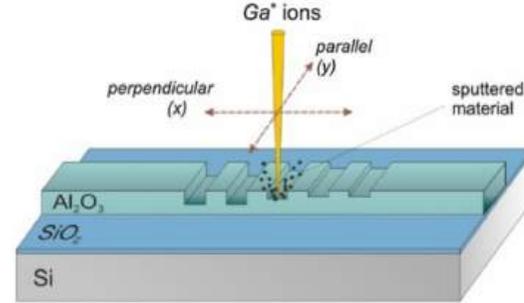
Electroactive species (eg. CuCl) are ionized in an electric field. The dissolved metal ions (eg. Cu^{2+}) are reduced at the cathode to solid atoms (eg. Cu) and form a deposit.

Localized Electrochemical Deposition

In the LECD the current required for electrodeposition is confined onto a sharp tip. By moving the tip in the desired trajectory, material from the electrolyte can be grown (deposited) along the trajectory of the tip.



Similar setup to SEM but heavy ions instead of electrons. The ion beam is used for etching. Large ions don't penetrate into the substrate.



Subtractive Processes

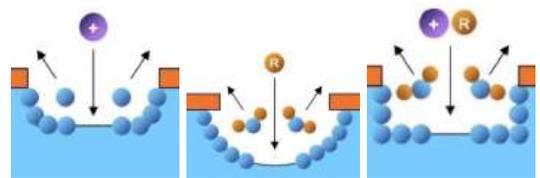
Wet Etching



the etch reactants come from a liquid source, High selectivity and low anisotropy, High etch rate, Often used for sacrificial layer etching.

- Isotropic etchants etch in all directions at the same rate. (<50°C)(Acidic)(Etching is fast, Undercuts mask)
- Anisotropic etchants etch at different rates depending on the orientation. (>50°C) (Alkaline) (Reaction rate slower/limited, does not undercut mask) (<111> slowest, <100> fastest direction)

Dry Etching



- Sputter etching: Physical etching by high energy bombardment
- Plasma etching: Chemical etching by reaction between gas molecules and sample surface.
- Reactive ion etching: Combination physical and chemical mechanism.
- Usually slower

FIB: Focused Ion Beam

Laser Machining

3-D Laser Lithography

3-D drawing of structures is created on computer, The laser writes the structure onto the photoresist, Direct laser writing (resolution 150nm for x,y and 450nm for z), Resist is developed to give the final structure, the structure can act as a mold for further deposition of material. Is the same as two photon polymerization. It is compatible with positive and negative photo resist. It utilizes femtosecond lasers.

Self-assembly

Static Self-assembly

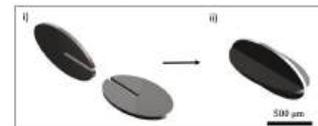
Systems are at global or local equilibrium, Do not dissipate energy, Formation of the ordered structure may require energy (for example in the form of stirring), but once it is formed, it is stable.

Dynamic Self-assembly:

The interactions responsible for the formation of structures between components only occur if the system dissipates energy.

Example of Design problem

Task 1: You want to fabricate a microrobot to treat inflammatory stomach diseases. The design consists of two identical magnetic plates (i), which are assembled to form the microrobot (ii). Give the fabrication steps starting with a plain silicon wafer up to the metallic assemblies and explain each of the steps in a short sentence.



Solution 1: 1) Copper layer deposition using PVD 2) Photolithography to create a photoresist mold with the desired shape 3) Electroplating magnetic material (e.g. Nickel) into mold 4) Lift-off (removal of photoresist) 5)

Wet etching of sacrificial copper layer to release the metallic assemblies

Task 2: In order to treat the inflammation, you want your microrobot to transport as much drug as possible. Describe two ways how you can increase the amount of drugs per microrobot. (one sentence each)

Solution 2: Etch microrobot to make it porous (increasing of surface throughout microrobot). Coat microrobot with porous polymer or liposomes, able to absorb the drug.

Case Study

a) Deposit Sacrificial Copper Layer



b) Apply Photoresist Mold



c) Electroplate Nickel into Mold



d) Strip Photoresist



e) Etch Sacrificial Copper to Release Nickel Parts



- a) A few hundred nm of copper are deposited on silicon by PVD technique
- a) Copper forms the conductive layer onto which the metallic microrobot body parts will be deposited
- a) It is called the sacrificial layer because it will finally be etched away or «sacrificed» to get free metallic microrobot parts
- b) A negative photoresist is spin-coated onto the copper
- b) The resist is developed using photolithography
- b) This leaves behind microrobot-shaped areas on the copper separated by islands of photoresist
- c) The wafer is now connected to the cathode of an electrochemical bath
- c) A suitable electrolyte containing nickel, and a suitable current density are chosen for the electro-deposition
- c) The nickel from the electrolyte gets deposited onto the conductive copper in between the photoresist islands

- d) The photoresist is now stripped from the wafer
- d) This leaves microrobot shaped planar parts sticking on top of the copper
- e) The wafer is now dipped into a chemical solution which selectively etches the copper
- e) The etching of copper is isotropic
- e) This frees the nickel parts from the copper underlayer. The planar parts are then assembled to get a 3-D shape

Nanofabrication

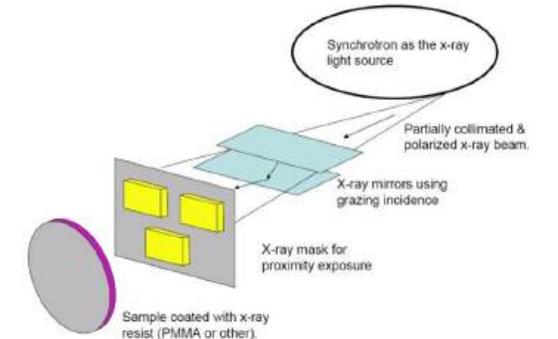
Extreme UV () Lithography

λ 13.5nm state of art. Advantages: extend minimum line width up 7nm without throughput loss. Minimum Linewidth: 30nm.

Disadvantages: UV is strongly absorbed in all materials, therefore lithography process must be performed in vacuum, Special masks (multilayer silicon or glass) and mirrors are needed, Extensive (ex. Light source). Complex masks needed.

X-Ray Lithography

X-ray(1nm) generated by a synchrotron storage ring is used as the energy source, As most materials have low transparency at λ 1nm, the mask substrate and pattern must be thin (1-2 μ m thick for mask; 0.5 μ m for pattern). Complex mask fabrication due to stress on thin mask.

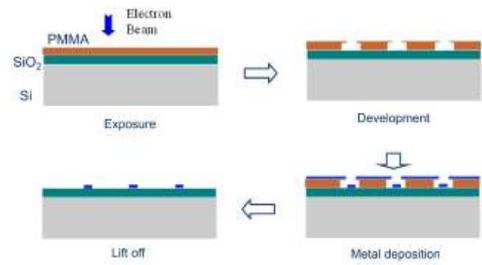


E-Beam Lithography

Uses Electrons to expose electron-sensitive resist. Not limited by wavelength of light. Theoretical resolution down to 1Angstrom. Currently main technique used for nano structures. Patterns are directly written into the resist by a scanning EBeam (SEM).

Disadvantages: Electron scattering in the resist and the substrate limit the theoretical resolution. 100Angstrom (0.01 μ m) e-beam becomes 0.2 μ m line.

Lift-off process:



AFM based Exposure and Lithography

Exposure of resist using electrons from a biased AFM tip (non-contact mode). Similar resists can be used as for e-beam.

A heated cantilever tip directly evaporates the thermally responsive resist. The directly written shapes reflect the geometry of the cantilever tip. High speed, micro-second exposure time.

Advantage of using the AFM: Detailed imaging of the substrate, Precise alignment between substrate and electron beam.

Microorganisms and Bio-inspired Robotics

Biorobotic Definitions

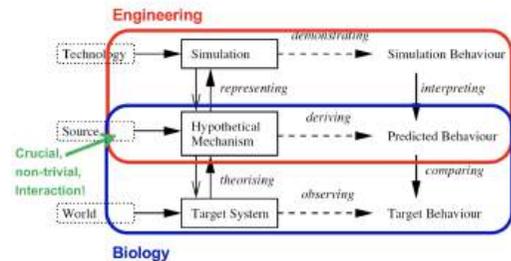
Biomimetics: An engineered device that reproduces exactly the target biological system.

Bioinspired: An engineered device that has borrowed some concept of biology, but has taken some freedom in its implementation.

Biological robots: An emulation of a biological system used to better understand the biological system itself.

Engineering Steps

Step 1: Identify the Target Behavior. Step 2: Model the Target Behavior. Step 3: Implement and Validate an Artificial Version of the Model.



Two key points: Spatiotemporal scale differences. Level of abstraction.

Swimming vs Flying

$\rho_w = 998.2 \frac{kg}{m^3}$, $\rho_a = 1.2 \frac{kg}{m^3}$, $\mu_w = 10^{-3} \frac{N \cdot s}{m^2}$, $\mu_a = 1.82 \cdot 10^{-5} \frac{N \cdot s}{m^2}$ Inertial and viscous forces are 10-1000 times higher in swimming. (More speed in air to generate sufficient forces.) Reynolds numbers of swimming is 15 times larger than for flying. Microflyers have similar Re to certain swimmers, but buoyancy is much stronger for swimmers due to ρ_w . Temporal frequencies are much higher for flying.

Bioinspired Microrobots in fluids

Flagella rotating, helical propulsion. Flagella beating, planar waves. Cilia, back and forth beating. **Flagella Motor:** Driven by a rotary engine. Powered by proton motor force. 200 to 1000 rpm. **Chemotaxis Strategy:** $\langle x^2 \rangle = 2Dt$. E.coli have mixed receptor clusters. Swimming is more frequent as the bacterium approaches a chemoattractant (food). Tumbling is more frequent further away from the food. Depending on the rotation direction, several flagella either form a bundle and swim forward or they repel each other, stop swimming, and start tumbling.

Step-out frequency ω_{max} : The maximum rotational speed ω_{max} and the maximum velocity u_{max} of the Artificial Bacterial Flagellum (ABF) is limited by the maximum available magnetic torque. If the frequency is larger, it can no longer follow the rotation. (Possible method to switching of individual robots)

The step out frequency is defined as $\omega_{step-out} = \frac{a}{ac-b^2} \tau_{max}$ It can be influenced by the head size.

Challenges for Biomedical Robots

Robotics and Medicine

The classical approach: Large extra-corporeal robots and tools. Minimally Invasive procedures. Advantages to conventional surgery:

- Decreased invasiveness (less trauma, fast recovery)
- Higher specificity (reduced side effects)
- New treatments possible (advanced functionality)

Limitations of Microsurgery: Surgical microscopes. Resolution (30 μm). Visible light. Human sensory-motor performance: Precision (15-20 μm). Dexterity (Fingerfertigkeit). Force/tactile sensitivity.

Important Characteristics of Biomicrobots

Propulsion: Ability to move, autonomously or with external guidance.

Localisation: Ability to be pinpointed inside the body.

Biocompatibility: Ability to discharge their functions without harming the body.

Functionality: Deliver a payload or detect the presence of a substance.

Biomedical Microrobots: Tracking

Necessary to know the location of the microrobot in the body.

Common issues: Spatial resolution, Noise rejection, Dependency on material properties, Adequate refresh rate.

Visual Tracking: In areas of the body where an optical image is available (Outer ear, Eye). Uses off-the-shelf components (Camera, Lenses, Microscopes).

Electromagnetic tracking: Pair of devices (Fieldgenerator, sensor). Low-frequency (non-radiating) field induces a voltage difference on sensor (Voltage as a function of distance). Accuracy depends on material properties, shape and sizes and position of nearby objects.

Magnetic tracking: A magnet is incorporated on the device to be localized, Array of magnetoresistive or Hall sensors used to measure the field, Offsetting earth's field, Assumption: the magnet behaves like a point-dipole (accurate for spheres), Promising technique where line-of-sight is not an issue, The body is "transparent" to low-frequency magnetic fields, However, we need to solve a non-linear equation calculate the position, Usually, calibration is needed

Ultrasound Localisation: Main Methods: Time difference of arrival (TDOA), Phase shift (PS). Advantages: Good resolution, Minimal risk, High speed, adequate frame rates, low cost. Disadvantages: Low signal-to-noise ratio. Strong wave reflector(e.g. Bones)

Biomedical Microrobots: Biocompatibility:

Depends on the localization on the body, length of time (Short-term and long-term biocompatibility), characteristic of the material (Chemical composition, Surface topography: smooth/porous, Surface energy: hydrophobic/ hydrophilic, Grain structure: Fine/coarse, Crystallinity: crystalline/amorphous). Properties change in micro and nano scales.

Imparting Biocompatibility:

Treating the surface to render it biocompatible.

Coating the surface with a biocompatible material.

Coating: Stainless steel (medical grade): Used for surgical instruments. Difficult to coat. Gold: Easy to coat, but expensive. Titanium: Low weight, ideal for implants. Less expensive and easy to coat. 3D printable. Polymer coating: Large number of biocompatible polymers available. Applying by directly in the polymer form or indirectly in the form of monomers. Conductive polymers can be "tuned". Electropolymerization (when electrical potential is applied). Can electrodeposited into specific shapes. Toxic materials are amongst the materials that lead to inflammation (others include carbon etc.).

Determining Biocompatibility:

Short term:

Cytotoxicity tests: Cells from human body are cultured

on the material. Contain fluorescent dye. Rate of cell growth and cell death is monitored.

Tissue culture tests: Material is implanted in vitro in tissue culture from the region of the body where the material is to be implanted. The effects of the histology of the tissue is monitored.

Long term:

Animal testing: Implant the material in group of animals. Clinical trials on human beings: Immune response of the body is multifaceted. Only broad assessments of biocompatibility are possible.

Application of Microrobots in Medicine

Targeted Therapy

Drug Delivery: Without microrobotics the whole body sees the drug through bloodstream. Targeted delivery with microrobot can reduce side effects and ensure high drug concentration.

Stem Cell Delivery: Similar to drug delivery, but cells need special condition to survive. Strategies: Cells attach on microrobot, internal capsule for cells, cells modified into a "robot".

Thermal Energy: Hyperthermia: moderately raise temperature to 40-45 $^{\circ}C$, improve effectiveness of chemotherapy/radiotherapy. Thermoablation: Raise to 50 $^{\circ}C$, kill cells. raising temperature: High frequency magnetic fields. Motion and friction dissipates heat. Eddy current in conductive material. Ultrasonic-resonating mechanical materials.

Radiation: Brachytherapy: Radioactive seed placed near unwanted tissue and kill cells.

Electrical Stimulation: Deep Brain Stimulation: Placing tiny electrodes on very specific locations in the brain. Electric stimulation can be achieved with magnetoelectric materials, enable to generate polarization with an eternally applied magnetic field. Stimulation of piezoelectric materials using ultrasonic vibration.

Targeted Therapy

Sensing and Marking: Remotely sensing biological data: Camera images from inside the body, pH and temperature digestive tract, oxygen concentration in the eye.

Optical Microscopes(0.2 μm), Fluoroscopy(100 μm), MRI(500 μm), Ultrasound (800 μm), Electromagnetic/Magnetic(100 μm).

Material Removal

Ablation and Biopsy You can only control so many degrees of freedom with magnetic actuation. Solutions: Passive motion through GI tract. Magnetic activation for sampling. Active motion using magnetic actuation. Passive sampling with environmental stimuli (pH responsive material).