"Nanotechnologie II" Sommersemester 2017

C. Ausgewählte Kapitel zur Nanotechnologie

- 7. Nanostrukturen durch Selbstorganisation
 - 7.1 Voraussetzungen für Selbstanordnung
 - 7.2 Thermodynamische Aspekte der Selbstanordnung
 - 7.3 Weitere Beispiele
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 - 8.1 Festkörper in reduzierter Dimension
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 - $8.3 \ {\rm Kohlenstoff-Nanor\"ohrchen}$
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 - 9.1 Einzelladungseffekte
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 - 9.3 Quanten-Computing
 - 9.4 Molekulare Elektronik
- 10. Nanooptik
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- 11. Nanotribologische Systeme
 - 11.1 Der Lotus-Effekt
 - 11.2 Der Gecko-Effekt
- 12. Biologische Nanostrukturen
 - $12.1\,$ Abbildung und mechanische Eigenschaften lebender Zellen
 - 12.2 Biologische Nanostrukturen

Literatur zur Vorlesung "'Nanotechnologie II"'

Zur Vorbereitung der Vorlesung wurde verwendet:

- Rainer Waser (Ed.) Nanoelectronics and Information Technology 2nd edition, John Wiley & Sons Ltd 2005 ISBN 3-527-40363-9 (Standort UB: nach 8.20, 2003 E 201(2)f)
- S. M. Lindsay Introduction to Nanoscience Oxford University Press 2010 ISBN 978-019-954421-9
- Claire Dupas, Philippe Houdy, Marcel Lahmani (Eds.) Nanoscience
 Springer, Berlin 2004
 ISBN 3-540-28616-0
 (Standort UB: nano 0, 2007 A 4151)
- Günter Schmid (Ed.) Nanoparticles Wiley-VCH, Weinheim 2004 ISBN 3-527-30507-6 (Standort UB: nano 2, 2004 A 8753)
- Lukas Novotny und Bert Hecht *Principles of Nano-Optics* Cambridge University Press 2006 ISBN 978-0-521-83224-3 (Standort UB: phys 4.29, 2007 E 1379)
- Bharat Bushan (Ed.) Springer Handbook of Nanotechnology 2nd edition, Springer Berlin 2007 ISBN 3-540-29855-X

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Konvergenz von top-down- und bottom-up-Nanotechnologien.



Whatmore R W Occup Med (Lond) 2006;56:295-299

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Versuchsanordnung zur kontrollierten Abscheidung von Langmuir-Blodgett-Filmen



Versuchsführung bei der Abscheidung von Y-Typ von Langmuir-Blodgett-Filmen



Dendrimer mit eingeschlossenem Farbstoff-Radikal

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Dendrimer encapsulating dyes

Licht-zu-Ladung-Konverter



Light-to-charge converter

(Courtesy of Professor Devens Gust of Arizona State University.)

Nano-Muskel: Aktuator auf Rotaxane-Basis

(Reprinted with permission from Y. Liu, A.H. Flood, P.A. Bonvallet, S.A. Vignon, B.H. Northrup, H-R Tseng, J.O. Jeppesen, T.J. Huang, B. Brough, M. Baller, S. Maganov, S.D. Solares, W.A. Goddard, C-M Ho, and J.F. Stoddart, J. Am. Chem. Soc. 2005, **127**, 9745, Published 2005 by American Chemical Society).



"Nano-muscle" actuator based on rotaxanes

Attacking agents

- Nucleophiles give 2 electrons to cause heterolytic cleavage
- Electrophiles take two electrons
- Free radical reactions give 1 electron to each section of a homolytic cleavage
- Note that electrons can transfer around organic rings (pericyclic), e.g. in benzene
- Acid-base reactions, e.g. HCl gas dissolving in water to form hydrochloric acid

Einige nützliche Reaktionen



Protection/deprotection



- •BOC = *t*-ButylOxyCarbonyl
- Protects against nucleophiles
- Easily removed with acids

Beispiele für schwache Wechselwirkungen



10

Ein "Zwitterion": Unpolares Molekül wird in Wasser zum polaren Molekül



Amphiphile Moleküle: Moleküle mit hydrophoben und hydrophilem Ende

Bsp.: Phospholipidmoleküle mit hydrophiler Phosphat-Kopfgruppe und hydrophobem paarigen Schwanz aus Alkanketten (CH₂)



Selbstaufbauende amphiphile Strukturen



Bilayer sheet

(From Molecular Cell Biology, 4th ed. By H. Lodish, A. Berk, S.L. Zipursky, P. Matsudara, D. Baltimore, J. Darnell. © 2000, W.H. Freeman and Company. Used with permission)

Simulation der Formierung eines Vesikels



(Reprinted with permission from Molecular dynamics simulation of the spontaneous formation of a small DPPC vesicle in water in atomistic detail, A.H de Vries et al., A.E. Mark, and S.J. Marrink, J. Am. Chem. Soc. 2004 **126**: 4488. Published 2006 by American Chemical Society)

- Packing effects depend on geometry
- Non-spherical micelles
- Spherical micelles
- Vesicles/bilayers





Bilayer sheet





 $\boldsymbol{\ell}_{\rm c}\,$ is the length of the hydrocarbon chain

 ${\cal V}\,$ is the volume occupied by the hydrocarbon chain ${\cal A}_{\!\scriptscriptstyle {\cal O}}$ is the area of the head group

Beispiel für eine Lipid-Doppelschicht: Das Mitochondrium



(EM image is reproduced with permission from Chapter 4 of The genetic basis of human disease by G. Wallis published by the Biochemical Society 1999. Copyrighted by the Biochemical Society. <u>http://www.biochemj.org.</u>)

Pyruvate oxidation – 30 ATPs vs 2

Beispiel für SAM



Self-assembled monolayers (SAM)



(Reproduced with permission from Functional molecules and assemblies in controlled environments, Weiss, P.S. published by Accounts of Chemical Research, 2008, courtesy of Professor Paul Weiss.)



Bond fluctuations

(From A bond-fluctuation mechanism for stochastic switching in wired molecules, G.K. Ramachandran, T.J. Hopson, A.M. Rawlett, L.A. Nagahara, A. Primak and S.M. Lindsay, Science 2003, 300, 3413. Reprinted with permission AAAS. Readers may view, browse and/or download material for temporary copying purposes only, provided that these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published or sold in whole or part without prior written permission from the publisher.)

Beispiel für die Anwendung von SAMs: Biopatterning von Proteinen Array zur Untersuchung <1000 Antikörper (links) und einzelner Moleküle (rechts)



Dip-Pen-Nanolithografie



Figure 4.3

Schematic of the dip pen lithography process—the wiggly lines are molecular "ink."

Courtesy of the Mirkin Group, Northwestern University.



Quantum dots from 2 phase synthesis with Ostwald ripening

(Reprinted with permission from Synthesis and characterization of nearly monodisperse CdE (E=S,Se,Te) semiconductor nanocrystallites, C.B. Murray, D.J. Noms and M.G. Bawendi, J. Am. Chem. Soc. 115 8706 Published 1993 by American Chemical Society).

Kinetisch getriebene Prozesse: Ausfällung von Nanopartikeln aus der Gasphase



Figure 1. Schematic of VLS growth of Si nanowires (SiNWs). (a) A liquid alloy droplet AuSi is first formed above the eutectic temperature (363 °C) of Au and Si. The continued feeding of Si in the vapour phase into the liquid alloy causes oversaturation of the liquid alloy, resulting in nucleation and directional nanowire growth. (b) Binary phase diagram for Au and Si illustrating the thermodynamics of VLS growth.

Si Nanowires from Au/Si eutectic seeded on Au NanoParticles

(Reproduced with permission from Semiconductor nanowires, W. Lu and C.M. Lieber J. Phys. D: Applied Physics 2006 with permission from IOP publishing and courtesy Wei Lu.)





(Courtesy of Professor Hao Yan, Arizona State University)



(Courtesy of Professor Hao Yan, Arizona State University)





(Reprinted by permission from McMillan Publishers Ltd.: Nature Publishing Group, Folding DNA to create nanoscale shapes and patterns, P. Rothmunde, <u>Nature</u> 2006, **440**, 297.)





Figure 2 | DNA origami shapes. Top row, folding paths. a, square; b, rectangle; c, star; d, disk with three holes; e, triangle with rectangular domains; f, sharp triangle with trapezoidal domains and bridges between them (red lines in inset). Dangling curves and loops represent unfolded sequence. Second row from top, diagrams showing the bend of helices at crossovers (where helices touch) and away from crossovers (where helices bend apart). Colour indicates the base-pair index along the folding path; red is the 1st base, purple the 7,000th. Bottom two rows, AFM images. White lines and arrows indicate blunt-end stacking. White brackets in **a** mark the height of an unstretched square and that of a square stretched vertically (by a factor >1.5) into an hourglass. White features in **f** are hairpins; the triangle is labelled as in Fig. 3k but lies face down. All images and panels without scale bars are the same size, 165 nm × 165 nm. Scale bars for lower AFM images: **b**, 1 µm; **c**–**f**, 100 nm.

(Reprinted by permission from McMillan Publishers Ltd.: Nature Publishing Group, Folding DNA to create nanoscale shapes and patterns, P. Rothmunde, <u>Nature</u> 2006, **440**, 297.)

Partikuläre Nanostrukturen



Abb. 2 Der "Lycurgus-Kelch" aus dem 4. Jahrhundert erscheint im reflektierten Licht grün. Wird er jedoch von innen beleuchtet, dann erstrahlt er in einem satten Rot.



Abb.1 Je nach der Größe der sphärischen Gold-Cluster im Lösung smittel variiert der Farbeindruck.

Eines der farbenprächtigen Fenster der St. Nicolai-Kirche in Kalkar. Bei seinen Entwürfen ließ sich der Künstler Karl-Martin-Hartmann von physikalischen Motiven inspirieren.⁹

Partikuläre Nanostrukturen



Abb. 1:

Unterschiedlich große CdSe-Nanopartikel in Lösung lassen sich mit UV-Licht zur Emission in den verschiedensten Farben anregen.



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Physik Journal 3 (2004) 118
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Abb. 2:

Das Energiespektrum eines Quantenpunkts (Mitte) liegt zwischen dem eines Moleküls (links) und dem eines Festkörpers (rechts). Die Energiezustände sind diskret und man spricht vom niedrigsten unbesetzten bzw. höchsten besetzten Molekül-Orbital (LUMO bzw. HOMO)



Abb. 3:

Durch nasschemische Verfahren lassen sich Halbleiter-Nanopartikel in Gramm-Mengen herstellen. Die Elektronenmikroskop-Aufnahme zeigt einen 6nm großen, einkristallinen CdSe-Nanokristall mit einer facettierten Oberfläche.



TEM-Aufnahme von kristallinen TiO₂-Teilchen (dunkel) mit einem Diketopyrrolopyrrol-Pigment (hell, größer) in einem Bindemittel. In höherer Vergrößerung (Inset) lässt sich sogar die Kristallstruktur und die Beschichtung eines TiO₂-Nanopartikels erkennen. (Foto: Sachtleben)

Physik Journal 3 (2004) 118

Festkörper in reduzierter Dimension

	d = 3	d = 2	d = 1	d=0
$\epsilon(\vec{k})=$	$\frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2\mathrm{m}^*}$	$\frac{\hbar^2(k_x^2+k_y^2)}{2\mathrm{m}^*}+E_{\mathrm{m}}$	$\frac{\hbar^2 k_x^2}{2m^*} + E_m + E_n$	$E_m + E_n + E_l$
		"Quantenfilm"	"Quantendraht"	"Quantenpunkt"

	Metall	2-dimensionales Elektronengas (z.B. GaAs)	Quantenpunkt (z.B. GaAs) "künstliches Atom"	Atom
Ausdehnung	1 cm ³		(10 nm) ³	0.1 nm
charakteristische Wellenlänge	$\lambda_{\rm F} \sim 0.5 \ {\rm nm}$	$\lambda_{\rm F} \sim 10-50 \ {\rm nm}$	a* = 10 nm	$a_{\rm B} = 0.05 \ {\rm nm}$
Energieskala	ε _F ~ 5 eV	$\epsilon_F \sim m eV$	$\Delta \epsilon \sim m eV$	Δε ~ 10 eV
Anregungsenergie	10 ⁻¹⁰ eV	~ meV z-Quantisierung	~meV	~ 10 eV



Nanokristalline Materialien



2

http://sic.epfl.ch/publications/SCR02/scr13 page9e.html

Elektronischer Transport im ausgedehnten Festkörper: semiklass. Beschreibung



Leitwertquantisierung



Aharonov-Bohm-Effekt



| 1/ AH |

Fig. 1. (a) Resistance as a function of magnetic field obtained at 60 mK for an Au ring 0.825 µm average diameter and 0.041 µm line width. Arrows indicate the conductance scale in units of e^2/h . (b) Fourier transform of the data displayed above with arrows indicating the expected frequency range for h/eand h/2e oscillations as well as the scale for the aperiodic background fluctuations predicted by Stone for this ring. The inset is an electron micrograph of this ring.

Quelle: Webb et al. JMMM, 54, 1423 (1986).



Quelle: R. Häussler, Dissertation Karlsruhe
Schwache Lokalisierung und Universelle Leitwertfluktuationen (UCF)



Quelle: E. Scheer, Dissertation Karlsruhe

Leitwertstufen : Leitwert wird durch Transportkanäle bestimmt



Quelle: Scheer et al. Nature 394, 154(1998).



Spin-Ladungs-Entkopplung in 1D antiferromagnetischer Kette



Eindimensionale monoatomare Metallketten



Co auf vicinalem Pt (111)



Au auf vicinalem Si (111)

Quelle: Gambardella et al. Nature 416, 301 (2002).

Eindimensionale Halbleiter-Strukturen hergestellt durch "Cleaved-Edge-Overgrowth"



Fullerene





Kohlenstoff- Nanoröhren









Herstellung von Kohlenstoff- Nanoröhren







Aufrollvektor (n,m): $C_h = na_1 + ma_2$

W. Hönlein, F. Kreupl, Physik Journal 3, 39 (2004)



Abb. 2:

Der Aufrollvektor (n,m) der Nanoröhrchen ist über die Basisvektoren a_1 und a_2 des Grafitgitters definiert. Je nach Konfiguration können die Röhrchen metallisch oder halbleitend sein (b, vgl. Text).

98 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0

(4.2) (8.2)

14.40

zigžag

(5.4) (8.4) (7.4)

10.51

(2.3)

30

(R.2) (R.2)

1.11 (2.1) (3.12

4

me tallisch

he lok it nd

Geometrische Struktur von Kohlenstoff- Nanoröhren



2D Dispersionsrelation von Graphen





A. Geim, A.H. MacDonald Phys. Today **60**, 35 (2007)





2D-Dispersionsrelation von Kohlenstoff-Nanoröhren

metallisch: (3,3) CNT 8 (c) (a) (b) 8 4 4 W - WF [eV] 0 W-WF [eV] k_x 0 -4 -8 -4 k_v -8 k_x ky k_x π/P -π/P

halbleitend: (4,2) CNT



2D-Zustandsdichte von Kohlenstoff-Nanoröhren



Damaszenerstahl mit Kohlenstoff-Nanoröhren und Cementite Fe₃C-Nanodrähten



Vertikale Verbindung zwischen zwei Leiterbahnen aus Bündeln von mehrwandigen CNT



aus einzelnen mehrwandigen CNT



Planarer Feldeffekttransistor





Konzept eines vertikalen Feldeffekttransistor





Mechanische Eigenschaften von Kohlenstoff-Nanoröhrchen

Material	Young's	Tensile
	Modulus (GPa) Strength (GPa)	
SWNT	1054	150
SWNT bundle	1054	75
MWNT	1200	150
Diamond	1000	1.2
Steel	200	0.4
Copper	110	0.413
Ероху	3.5	0.005
Wood	16	0.008

Electrical	Thermal	Density (g/cm3
Resistivity (Ωm)	conductivity (W/mK)	
10-6	1750 - 5800	1.3
0.1-10 ⁻³	35	
10 ⁻⁶	>3000	2.6
1.0x10 ¹² - 1.0x10 ¹⁴	1000 - 2600	
12.0x10 ⁻⁸ - 170x10 ⁻⁸	43	7.8
1.70x10 ⁻⁸ - 2.65x10 ⁻⁸	390	
		4.25







Herstellung von Garnen aus Kohlenstoff-Nanoröhrchen

Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology, M. Zhang, K. R. Atkinson, & R. H. Baughman, *Science*, **306**, 1358, 2004.



Garne und funktionale Textilien aus Kohlenstoff-Nanoröhrchen



M.D. Lima et al., Science 331 (2011) 51

Herstellung von Clustern aus der Gasphase





SEM-Bild eines cubo-oktaedrischen Co-Clusters

Größenverteilung von Cluster



FIG. 1. Sodium cluster abundance spectrum: (a) experimental (after Knight *et al.*, 1984); (b) dashed line, using Woods-Saxon potential (after Knight *et al.*, 1984); solid line, using the ellipsoidal shell (Clemenger-Nilsson) model (after de Heer, Knight, Chou, and Cohen, 1987).

Heer et al. RMP 65, 611 (1993).

Herstellung von Clustern durch Reduktion von Metallionen

Space filling model of the molecular structure of $[Ag_{168}S_{66}(StC_5H_{11})_{36}(PP)_6]$ (PP: bidentate ligand).

Space filling model of the molecular structure of $[Ag_{274}S_{80}(SCH_2Ph)_{114}]$, (Ag: blue; S: yellow; P: green; C: light grey; H: grey).





 $[Ag_{262}S_{100}(tBuS)_{62}(Ph_2P(CH_2)_4PPh_2)_6]$



Größenabhängigkeit der Bindungsenergie



Schmelztemperatur für Au-Cluster



Größenabhängigkeit der Ionisationspotentials





FIG. 3. The small-particle electronic heat capacity as a function of temperature, taken from Denton, Mühlschlegel, and Scalapino (1973): (a) An average of the even and odd particle calculations; (b) the linear heat capacity for the continuum case, shown for comparison (dashed-dotted line). Note the displacement of the high-temperature asymptote by $-k_B/2$ consistent with Eq. (2.29).



FIG. 4. The small-particle magnetic susceptibility calculated by Denton, Mühlschlegel, and Scalapino (1973). The calculated spin susceptibilities are normalized to the Pauli value taken here to be $\chi_P = 2\mu_B^2/\delta$.

size effect in Metallclustern

Schema für die Einzelelektronenbox (SEB)



Stabiler Zustand für n Elektronen in der Box: $e(n-1/2) < C_G U < e(n+1/2)$

Quelle: G. Schön: Single-Electron Tunneling. In: Quantum transport and dissipation. Weinheim 1998. S. 149-212.

Coulomb-Treppe



Quelle: G. Schön: Single-Electron Tunneling. In: Quantum transport and dissipation. Weinheim 1998. S. 149-212. $\frac{3}{3}$

Schematischer Aufbau und realer SET





Schwellenspannung für einen symmetrischen SET ($C_L=C_R=C$) in Abhängigkeit von V_g :



Innerhalb der Rauten ("diamond shaped regions") ist der Stromfluss durch die Coulomb-Blockade unterdrückt, die Ladung auf der Insel ist stabil.

Colourplot der Coulomb-Blockade



Asymmetrischer SET



Quelle: K.K. Likharev: Single-Electron Devices and Their Applications. In: Proceedings of the IEEE, Vol 87, No.4, April 1999.



Strom-Kontur-Plot für Aluminium-SET mit e/C_{Σ} =0.1V bei T=4.2K



Quelle: K.K. Likharev: Sub 20-nm Electron Devices.

In: Advanced Semiconductor and Organic Nano-Techniques, Pt. 1. Academic Press, 2002.

Single electron transistor

Copyright Stuart Lindsay 2008



(From Excitation spectra of circular, few electron quantum dots, L.P. Kouvenhoven, T.H. Oosterkamp, M.W.S. Danoesastro, M. Eto, D.G. Austing, T. Honda and S. Tarucha, Science 1997, **278**, 1788. Reprinted with permission from AAAS. Readers may view, browse and/or download material for temporary copying purposes only, provided that these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published or sold in whole or part without prior written permission from the publisher.)

Resonantes Tunneln



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Josephson charge qubits



FIG. 1. A Josephson charge qubit in its simplest design formed by a superconducting single-charge box.



FIG. 2. The charging energy of a superconducting electron box is shown as a function of the gate charge n_g for different numbers of extra Cooper pairs n on the island (dashed parabolas). Near degeneracy points the weaker Josephson coupling mixes the charge states and modifies the energy of the eigenstates (solid lines). In the vicinity of these points the system effectively reduces to a two-state quantum system.

Quelle: Y. Makhlin et al., Rev.Mod.Phys. 73, 357 (2001).
Josephson charge qubits





FIG. 3. A charge qubit with tunable effective Josephson coupling. The single Josephson junction is replaced by a fluxthreaded SQUID. The flux in turn can be controlled by a current-carrying loop placed on top of the structure.

FIG. 4. A register of many charge qubits coupled by oscillator modes in the *LC* circuit formed by the inductor and the qubit capacitors.

Beispiel eines realen supraleitenden Qubits: Die Einzel-Cooper-Paar box



Quelle: Y. Nakamura, Yu. A. Pashkin and J. S. Tsai, Nature 398, 786-788(29 April 1999)



Funktionsweise der Einzel-Cooper-Paar box

Quelle: Y. Nakamura, Yu. A. Pashkin and J. S. Tsai, Nature 398, 786-788(29 April 1999)

Einzel-Cooper-Paar box: Kohärente Oszillationen



Quelle: Y. Nakamura, Yu. A. Pashkin and J. S. Tsai, Nature 398, 786-788(29 April 1999)

SQUID-Potential, level anti-crossing und experimenteller Aufbau eines flux qubits



b

Beispiel eines flux qubits mit 3 Josephson-Brücken



Konzepte molekularer Elektronik





Figure 14:

(a) Schematic presentation of a rectifying device based on an LB-film of the donoracceptor molecule 12.

(b) The I-V curve of the sandwiched LBmonolayer displaying rectifying character.



Figure 19: Scheme of a mechanically controlled break junction. On top of a bendable substrate a Au film is patterned with a freely suspended bridge in the center (see SEM micrograph in the middle panel). By bending the substrate in a three point support (lower panel: the pushing rod is driven by a motor), the Au bridge can be broken into two electrodes. By bending the substrate back and forth, the gap between the electrodes can be tuned with a distance resolution much better than Angstroms. This setup can be used to match the electrode gap precisely to the length of a molecule and finally to contact a molecule from two sides via well defined chemical S-Au bonds.

Molekulare Elektronik mit Bruchkontakten





Quelle: H.B. Weber et al.

- Wichtige Elemente zum Verständnis der I(V)-Kurven sind
 - Energieniveau-Diagramm mit der Lage der Fermi-Energie relativ zu LUMO und HOMO



- Verbreiterung der molekularen Niveaus aufgrund der Elektrodenkontakte

Molekulare Elektronik mit Bruchkontakten



"Super-Molekül" aus Atomen der Elektroden und dem eigentlichen Molekül

HOMO





Aspekte der Nano-Optik





2D photonischer Kristall

Bandstruktur eines 2D photonischen Kristalls

Beispiel eines 2D photonischen Kristalls



Taken from: R. Wehrsporn, U. Gösele et al., MPI Halle

Größenordnung der Gitterkonstante photonischer Kristalle

Spektralbereich	Frequenz [Hz]	Wellenlänge λ_0 [m]
Mikrowellen	$10^9 - 10^{11}$	$10^{-1} - 10^{-3}$
Infrarot	$10^{13} - 10^{14}$	$10^{-5} - 10^{-6}$
sichtbares Licht	10^{14}	10^{-6}
UV-Strahlung	$10^{15} - 10^{16}$	10^{-7}
Röntgenstrahlung	$10^{17} - 10^{19}$	$10^{-8} - 10^{-11}$

 \rightarrow Sub-µm-Skala für Bandlücken im Sichtbaren

Beispiele für photonische Defektstrukturen



Mikrokavität

Wellenleiter

Beispiele für 3D photonische Kristalle in der Natur

Ringelwürmer



10 µm

Quelle: Vucosic et al., Nature 424, 852(2003)



Blauer Morphofalter ^{1,3 µm}

Beispiele für 3D photonische Kristalle in der Natur



Beispiel für 3D photonische Kristalle in der Natur: Opale







Künstliche Opale



Colvin, MRS Bulletin 26(8), 637 (2001)

Künstlicher Opal: invertierter Si-Opal mit Bandstruktur



(111) Oberfläche des invertierten Si Opals



Vollständige Bandlücke bei λ_{0} = 1,5 μm



Plasmonen:

(Drude-)Dielektrizitätskonstante

Figure 12.1 Real and imaginary part of the dielectric constant for gold according to the Drude–Sommerfeld free-electron model ($\hbar\omega_p = 8.95 \text{ eV}$, $\hbar\Gamma = 65.8 \text{ meV}$). The solid line is the real part, the dashed line is the imaginary part. Note the different scales for real and imaginary parts.



Figure 12.2 Contribution of bound electrons to the dielectric function of gold. The parameters used are $\hbar \tilde{\omega}_p = 2.96 \text{ eV}$, $\hbar \gamma = 0.59 \text{ eV}$, and $\omega_0 = 2\pi c/\lambda$, with $\lambda = 450 \text{ nm}$. The solid line is the real part, the dashed curve is the imaginary part of the dielectric function associated with bound electrons.

Die Fresnel-Gleichungen



Figure 2.2 Reflection and refraction of a plane wave at a plane interface. (a) s-polarization, and (b) p-polarization.

Amplituden

$$E_{1r}^{(s)} = E_1^{(s)} r^s(k_x, k_y), \qquad E_{1r}^{(p)} = E_1^{(p)} r^p(k_x, k_y), E_2^{(s)} = E_1^{(s)} t^s(k_x, k_y), \qquad E_2^{(p)} = E_1^{(p)} t^p(k_x, k_y),$$

Reflexionskoeffizienten

Transmissionskoeffizienten

$$r^{s}(k_{x},k_{y}) = \frac{\mu_{2}k_{z_{1}} - \mu_{1}k_{z_{2}}}{\mu_{2}k_{z_{1}} + \mu_{1}k_{z_{2}}}, \qquad r^{p}(k_{x},k_{y}) = \frac{\varepsilon_{2}k_{z_{1}} - \varepsilon_{1}k_{z_{2}}}{\varepsilon_{2}k_{z_{1}} + \varepsilon_{1}k_{z_{2}}},$$
$$t^{s}(k_{x},k_{y}) = \frac{2\mu_{2}k_{z_{1}}}{\mu_{2}k_{z_{1}} + \mu_{1}k_{z_{2}}}, \qquad t^{p}(k_{x},k_{y}) = \frac{2\varepsilon_{2}k_{z_{1}}}{\varepsilon_{2}k_{z_{1}} + \varepsilon_{1}k_{z_{2}}}\sqrt{\frac{\mu_{2}\varepsilon_{1}}{\mu_{1}\varepsilon_{2}}}.$$

2

Oberflächenplasmonen



field normal to the surface. This combined character also leads to the field component perpendicular to the surface being enhanced near the surface and decaying exponentially with distance away from it (b). The field in this perpendicular direction is said to be evanescent, reflecting the bound, non-radiative nature of SPs, and prevents power from propagating away from the surface. In the dielectric medium above the metal, typically air or glass, the decay length of the field, δ_a , is of the order of half the wavelength of light involved, whereas the decay length into the metal, δ_m , is determined by the skin depth. c., The dispersion curve for a SP mode shows the momentum mismatch problem that must be overcome in order to couple light and SP modes together, with the SP mode always lying beyond the light line, that is, it has greater momentum (hk_{sp}) than a free space photon (hk_0) of the same frequency ω .



There are three characteristic length scales that are important for SP-based photonics in addition to that of the associated light. The propagation length of the SP mode, δ_{so} , is usually dictated by loss in the metal. For a relatively absorbing metal such as aluminium the propagation length 2 µm at a wavelength of 500 nm. For a low loss metal, for example, silver, at the same wavelength it is increased to 20 µm. By moving to a slightly longer wavelength, such as 1.55 µm, the propagation length is further increases towards 1 mm. The propagation length sets the upper size limit for any photonic circuit based on SPs. The decay length in the dielectric material, δ_{ij} , is typically of the order of half the wavelength of light involved and dictates the maximum height of any individual features, and thus components, that might be used to control SPs. The ratio of δ_{sp} : δ_{sp} thus gives one measure of the number of SP-based components that may be integrated together. The decay length in the metal, δ_{m} , determines the minimum feature size that can be used; as shown in the diagram, this is between one and two orders of magnitude smaller than the wavelength involved, thus highlighting the need for good control of fabrication at the nanometre scale. The combinations chosen give an indication of range from poor (AI at 0.5 µm) to good (Ag at 1.5 µm) SP performance.

Oberflächenplasmonen: relevante Längenskalen

Quelle: Barnes et al., Nature 424, 824 (2003)

Oberflächenplasmonen



field normal to the surface. This combined character also leads to the field component perpendicular to the surface being enhanced near the surface and decaying exponentially with distance away from it (b). The field in this perpendicular direction is said to be evanescent, reflecting the bound, non-radiative nature of SPs, and prevents power from propagating away from the surface. In the dielectric medium above the metal, typically air or glass, the decay length of the field, δ_d , is of the order of half the wavelength of light involved, whereas the decay length into the metal, δ_m , is determined by the skin depth. c, The dispersion curve for a SP mode shows the momentum mismatch problem that must be overcome in order to couple light and SP modes together, with the SP mode always lying beyond the light line, that is, it has greater momentum $(\hbar k_{sp})$ than a free space photon $(\hbar k_0)$ of the same frequency ω .

Dispersionsrelation von Oberflächenplasmonen



Figure 12.6 Excitation of surface plasmons. (a) Close-up of the dispersion relation with the free-space light line and the tilted light line in glass. (b) Experimental arrangements to realize the condition sketched in (a). Left: Otto configuration. Right: Kretschmann configuration. L: laser, D: detector, M: metal layer.

Anregung von Oberflächenwellen in der Kretschmann-Konfiguration für Goldfilme verschiedener Dicke (in nm)



Box 3 Surface plasmon bandgaps



Periodic texturing of the metal surface can lead to the formation of an SP photonic bandgap when the period, a, is equal to half the wavelength of the SP, as shown in the dispersion diagram (a). Just as for electron waves in crystalline solids, there are two SP standing wave solutions, each with the same wavelength but, owing to their different field and surface charge distributions, they are of different frequencies. The upper frequency solution, ω_+ , is of higher energy because of the greater distance between the surface charges and the greater distortion of the field, as shown schematically in b. SP modes with frequencies between the two band edges, ω_+ and ω_- , cannot propagate, and so this frequency interval is known as a stop gap. By providing periodic texture in two dimensions, SP propagation in all in-plane directions can be blocked, leading to the full bandgap for SPs. At the band edges the density of SP states is high, and there is a significant increase in the associated field enhancement.

Anregung von Oberflächenplasmonen durch periodischer Gitterkoppler



Lokale Anregung von Oberflächenplasmonen durch verschiedene eingeschränkte Lichtfelder: (a) Sub-Wellenlänge-Öffnung, (b) bestrahltes Nanoteilchen, (c) fluoreszierende Moleküle

Anregung von Oberflächenwellen durch Sub-Wellenlängen-Öffnungen

cylindrical hole in a suspended Ag film (groove periodicity, 500 nm; groove depth, 60 nm; hole diameter, 250 nm; film thickness, 300 nm).



Anregung von Oberflächenwellen durch Sub-Wellenlängen-Öffnungen

parallel grooves on both sides of a suspended Ag film (slit width, 40 nm; slit length, 4400 nm; groove periodicity, 500 nm; groove depth, 60 nm; film thickness, 300 nm)



Streuung und Absorption von Licht durch Plasmonenmoden in kleinen Goldteilchen



Abb. 2 Der "Lycurgus-Kelch" aus dem 4. Jahrhundert erscheint im reflektierten Licht grün. Wird er jedoch von innen beleuchtet, dann erstrahlt er in einem satten Rot.

Der Lotus-Effekt

Nelumbo nucifera (lotus)



Colocasia esculenta



Fig. 50.35 SEM micrographs of two hydrophobic leaves, Nelumbo nucifera (lotus) and Colocasia esculenta

Quelle: Bushan, Nanotechnology, Springer 2003





Quelle: Wikipedia

Der Lotus-Effekt



Regentropfen perlen vom Blatt der Lotuspflanze (Nelumbo nucifera) einfach ab. Das liegt an der mikrofeinen Noppenstruktur auf der Blattoberfläche, die erst unter dem Rasterelektronenmikroskop (Inset) zu erkennen ist. (Quelle: W. Barthlott, Uni Bonn)



Bei Randwinkeln unterhalb von 90° (a) gilt eine Oberfläche als hydrophil und das Wasser breitet sich aus. Ist der Randwinkel dagegen größer als 90° (b), so spricht

man von hydrophoben Oberflächen, auf denen sich das Wasser zu Tropfen zusammenzieht und leichter abperlen kann.

Der Lotus-Effekt







Fig. 50.37 Contact angle for rough surface (θ) as a function of the roughness factor (R_f) for various contact angles for a smooth surface (θ_0) [50.173]





Superhydrophobizität ("Lotus-Effekt")

Der Lotus-Effekt beschreibt die Selbstreinigungsfähigkeit von Blättern.

Namensgeber ist die Lotuspflanze: Wasser perlt von ihrem Blättern ab, ohne sie zu benetzen.

Diese Eigenschaft nennt man hydrophob.

Auch einheimische Pflanzen wie die Kapuzinerkresse, die Akelei und der Kohlrabi zeigen diesen Effekt.



Blatt einer Akelei, Verschmutzung (durch Curry-Pulver simuliert) perlt mit Wasser einfach ab..

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www.kit.edu




Superhydrophobizität ("Lotus-Effekt")

Geranie (hydrophil)





Akelei (hydrophob)



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Superhydrophobizität ("Lotus-Effekt")

In Abhängigkeit vom Kontaktwinkel θ werden Oberflächen eingeteilt:



Durch Strukturierung können die hydrophoben Eigenschaften noch weiter verstärkt werden (Superhydrophobizität):





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10 000 × vergrößert

Blattoberfläche von Kapuzinerkresse

280 ×





Nanoskalige Wachsstruktur verstärkt hydrophobe Eigenschaften der Blattoberfläche \rightarrow Lotus-Effekt

Blattoberfläche einer getrockneten Kapuzinerkresse im Rasterelektronenmikroskop bei etwa 280- (links), 950- (Mitte) und schließlich 10 000-facher Vergrößerung (rechts). Zu erkennen ist die nanoskalige Wachsstruktur, der die superhydrophoben Eigenschaften der Kresse zugeschrieben werden.

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Environmental Scanning Electron Microscope (ESEM) im Laboratorium für Elektronenmikroskopie (LEM)

Im Gegensatz zu herkömmlichen Rasterelektronenmikroskopen können im ESEM Proben untersucht werden, die vorher nicht getrocknet und metallisiert werden müssen, was vor allem biologische Proben stark verändern würde. Es ist sogar möglich, auf der gekühlten Probe Wasserdampf zu kondensieren.



Untersuchung von Superhydrophobizität (Lotus-Effekt) bei der Kapuzinerkresse. Im ESEM wurde auf einem kleinen Blattstück Wasserdampf kondensiert, um die Tröpfchenbildung bei über 1000-facher Vergrößerung auf der Blattoberfläche zu beobachten.

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Zerstörung der Superhydrophobizität von Kapuzinerkresse

Durch Behandlung mit organischen Lösemitteln oder Seife kann die Wachsschicht auf den Blättern beschädigt werden. Die superhydrophoben Eigenschaften werden dadurch zerstört.



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Zerstörung der Superhydrophobizität von Kapuzinerkresse

Durch Behandlung mit organischen Lösemitteln oder Seife kann die nanostrukturierte Wachsschicht auf den Blättern beschädigt werden. Die superhydrophoben Eigenschaften werden dadurch zerstört.



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Der Lotus-Effekt



Fig. 50.38 (a) Formation of a composite solid–liquid–air interface for sawtooth and smooth profiles, and (b) destabilization of the composite interface for the sawtooth and smooth profiles due to dynamic effects. The dynamic contact angle $\theta_d > \theta_0$ corresponds to an advancing liquid–air interface, whereas $\theta_d < \theta_0$ corresponds to a receding interface [50.176]



Fig. 50.39 Optimized roughness distribution – hemispherically topped cylindrical asperities and pyramidal asperities with square foundation and rounded tops. The square base gives a higher packing density but introduces undesirable sharp edges [50.173]

Quelle: Bushan, Nanotechnology, Springer 2003

Der Lotus-Effekt



Fig. 50.40 (a) SEM micrographs of the patterned polymer surfaces. Both LAR and HAR are shown at two magnifications to see both the asperity shape and the asperity pattern on the surface. (b) Cartoon showing the effect of different radii on the patterned surface. Small radii can fit between asperities, while large radii rest on top of the asperities

Quelle: Bushan, Nanotechnology, Springer 2003



Fig. 50.41 Bar chart showing the contact angles for different materials and for different roughnesses [50.177]

Der Lotus-Effekt



Fig. 50.42 (a) Scale-dependent adhesive force for PMMA film versus PFDTES on PMMA film and PMMA HAR versus PFDTES on PMMA HAR (*top*), and (b) the effect of relative humidity on the adhesive force for PMMA film, LAR and HAR and for PFDTES on PMMA film and HAR [50.177]

Quelle: Bushan, Nanotechnology, Springer 2003

Haftsystem der Grünen Sauerampferkäfers (Gastrophysa viridula)





Attribution: James Lindsey at Ecology of Commanster





Haftsysteme in der Tierwelt

Fig. 1. Terminal elements (circles) in animals with hairy design of attachment pads. Note that heavier animals exhibit finer adhesion structures.



Fig. 2. Dependence of the terminal element density (N_A) of the attachment pads on the body mass (m) in hairy-pad systems of diverse animal groups ($\log N_A(m^{-2}) = 13.8 + 0.699 \log m(kg), R = 0.919$).

Quelle: E. Arzt, PNAS 100, 10603 (2003)

Kontakt zwischen einer Kugel und einem elastischen Halbraum...



...im Johnson-Kendall-Roberts-Modell

Der Gecko-Effekt



Fig. 4. Two cases of contact scaling. (a) Self-similarity: contact radius R scales with contact size s. (b) Curvature invariance: contact radius is independent of contact size.



Fig. 3. Interpretation of Fig. 2 in light of contact theory. A fit to all data (red line) gives a slope of $\approx 2/3$, corresponding to the self-similarity criterion. Within each lineage, a lower slope of $\approx 1/3$ is found, suggesting curvature invariance of the contacts with radius *R* (green lines). The approximate limit for such attachment devices (limit of maximum contact) is shown as a blue line.

Stenus bimaculatus (Kurzflügler)

http://www.kaefer-der-welt.de/stenus_bimaculatus_1.jpg



Haftsysteme in der Tierwelt

Quelle: L. Koerner, J. Insect Physiology 58, 155 (2012)

Fussabdruck des Käfers: Beispiel für Feuchthaftung



Fig. 4. SEM images of air-dried secretion prints left on the smooth surface (A) and on the surfaces with an asperity diameter of 0.3 µm (B), 3 µm (C), and 12 µm (D). Scale bar = 20 µm.

Der Gecko: Beispiel für Trockenhaftung





Figure 5. Geckos can recover from a fall by slapping a foot against a passing leaf or branch. This recovery takes advantage of the large adhesive forces that gecko toes are capable of generating. Consider the example of a 50-gram gecko that falls 10 centimeters before attaching a foot to a nearby leaf. During the fall, the gecko accelerates at 9.8 meters per second squared; at the instant it touches the leaf below, it will be moving at 1.4 meters per second. If the foot produces 5 newtons of friction, the gecko will come to a sudden stop (0.015 seconds) after sliding only 1.1 centimeters. This arrest uses 50 percent of the maximum shear capacity of one foot based on whole-animal measurements but less than 4 percent of the theoretical maximum calculated from single setae.

Quelle: K. Autumn, American Scientist 94, 124 (2006)

Der Gecko: Beispiel für Trockenhaftung



Figure 2. The structural hierarchy of the gecko adhesive system reveals different features at each scale. At the macro-level, a naked-eye view from behind a vertical glass window shows the tokay gecko (*Gekko gecko*) navigating that smooth surface with ease. A closer view of the bottom of the foot shows many ridges crossing each toe. The microstructure of a ridge reveals that it is covered with densely packed projections called setae, which are ordered in a neat, grid-like pattern. Each diamond-shaped structure is the branched end of a cluster of four setae. The fine microstructure of a single gecko seta shows individual fibrils of β -keratin, which comprise the shaft, and extensive branching at the end. The branched filaments form a nano-scale array of hundreds of flattened tips. (Photographs courtesy of Mark Moffett; electron micrographs courtesy of Stas Gorb and the author.)

Trockenhaftung vs. Feuchthaftung



Figure 4. The author measured the shear force (*left*) of a single seta by pressing it against a microsensor, then pulling perpendicular to the surface of the sensor. These data report the resulting force as a function of time. Inset diagrams show the relative positions of seta and sensor at different points in the experiment, with arrows to indicate the direction of force applied to the seta. The maximum observed force of 200 micronewtons was 32 times greater than the predicted value from animal experiments. At right, the author plotted attachment forces exerted by single setae as a function of the angle between the setal shaft and the surface. The results of two different types of experiments are shown: Filled symbols represent setae pulled away from the surface until they released; open symbols indicate setae held at a constant force as the angle increased. Each symbol shape represents a different seta. The data reveal a consistent angle of detachment—about 30 degrees—over the entire range of pulling forces.

Trockenhaftung vs. Feuchthaftung



Figure 7. The difference between polar surfaces and polarizable surfaces can be used to test the capillary and van der Waals hypotheses of gecko adhesion. For highly polarizable surfaces such as gallium arsenide (GaAs) and silicon dioxide (SiO₂), the capillary hypothesis (*a*) predicts that geckos will adhere strongly to the hydrophilic (polar) SiO₂ but not the hydrophobic (nonpolar) GaAs. The van der Waals hypothesis (*b*) predicts that the adhesive forces will be similarly large for both. Experiments that tested the adhesive force with whole animals on GaAs and SiO₂ surfaces (*c*) and with single setae on SiO₂ and silicon microsensors (*d*) showed comparable adhesion forces for both types of surfaces. These data match the predictions of the van der Waals hypothesis.

Trockenhaftung vs. Feuchthaftung



Figure 4. Dependence of the finite hair density of the attachment pads on the body mass in hairy pad systems of representatives from diverse animal groups. 1, 2, 4, 5: flies; 3: beetle; 6: bug; 7: spider; 8: gekkonid lizards. Adapted from Scherge and Gorb (2001). The systems located above the blue line rely on van der Waals forces (dry adhesion), whereas the systems below the line rely mostly on capillary and viscous forces (wet adhesion).

Adhäsive Mikrostrukturen



Figure 5. Patterned insect inspired polyvinylsiloxane surface. A: single structures are distributed on the surface according to the hexagonal pattern, in order to reach the highest packaging degree of single pillars (above aspect, SEM image). B: white-light interferometer image of single pillar head demonstrates an almost flat shape of the contacting surface. C: side aspect of the pillar array. D–F: behavior of structured PVS surfaces in contact with the glass surface (SEM images). The black arrowhead shows a dust particle in contact. Adapted from Gorb *et al* (2007).

Quelle: S. Gorb et al. Bioinsp.Biomim 2, S117 (2007)



Fig. 3. Photographs of a man attached to the glass ceiling (a) by a 20 cm × 20 cm PMMA plate covered by the mushroom-shaped adhesive microstructure (b), (c). (Photograph (a) is reprinted with permission from the press office of the University of Kiel).

Quelle: L. Heepe et al. Theo.&Appl. Mech. Lett. 2, 014008 (2012)

Aufbau einer Zelle



- Eukaryotische Zellen haben einen Zellkern, in welchem die Genexpression kontrolliert wird.
- Prokaryotische Zellen haben keinen Zellkern. Gene und Proteine befinden sich in derselben Hülle.

Anwendung der Rasterkraftmikroskopie in der Zellbiologie



Vorteil: Bilddarstellung unter physiologischen Bedingungen

Abbildung eines DNA-Stranges







Stützstrukturen (z.B. Actin) der Zelle werden sichtbar

z-Piezo Bewegung im Rückkopplungskreis Topografie -"wahre" Höheninformation

Cantilever Verbiegung

stellt Änderungen der Höhe dar

Kombiniertes AFM / optisches Mikroskop





Lichtmikroskop

AFM



Temperaturkontrolle

→ Abbildung lebender Zellen

Wechselwirkung von Fibroblasten mit einer extrazellulären Matrix (ECM)





Quelle: Carlos P. Huang, Lab Chip, 2009, 9, 1740–1748

Molekulare Struktur von Zell-Substrat Kontakten



Fibronectin, Laminin, Vitronectin	
Aktin	
lpha-Aktinin	
ß3-Integrin	
FAK	
Paxillin	
Phosphotyrosin	
Talin	
Tensin	
Vinculin	





Quelle: C. Chen et al., Science 276, 1425 (1997);

Formation hochgradig geordneter und paralleler Kollagen I Mikrofibrillen auf Glimmeroberflächen



Die Matrizen sind ~ 3 nm hoch





Konventionelle Kollagenmatrix

geordnete Kollagenmatrix

Hat die Kollagenmatrixtopografie einen Einfluß auf das Zellverhalten?

Gerichtete Wanderung von Fibroblasten auf nanostrukturierten Kollagenmatrizen





AFM image of a nanostructured collagen matrix

Fibroblasts migrate directionally on the collagen matrix

Anisotrope Deformation der Kollagenmatrix





anfängliche Matrixdeformation späte

späte Matrixdeformation

Zeitraffer AFM-Aufnahme lebender Zellen



Zellausrichtung durch anisotrope Deformation der Kollagen-Matrix



Hohe Zugfestigkeit
Herzschlag





Cardiomyocytes

Herstellung mikrostrukturierter Zellkultursubstrate durch direktes Laserschreiben (DLW)



AG Wegener AG von Freymann AG Bastmeyer²⁹

Quelle: Vorlesungsfolien Clemens Franz, CFN

Flexible 3D-Substrate



Quelle: Vorlesungsfolien Clemens Franz, CFN

Klein et al., Adv. Mater. 2010

Messung der Steifheit flexibler Zellkultursubstrate zur Abschätzung der zellulären Kontraktionskräfte





zelluläre Kontraktionskräfte: ~ 40 to 60 nN

Zweikomponentige Gerüste



Funktionalisierung des proteinabweisenden Gerüstes mit Ormocomp Würfeln

F. Klein, B. Richter et al., Advanced Materials 2011, 23, 1341

Zweikomponentige Gerüste

• Beschichtung mit Fibronectin und Zellbesatz



Zweikomponentige Gerüste

• dreidimensionale Kontrolle der Zellgestalt



F. Klein, B. Richter et al., Advanced Materials 2011, 23, 1341

A Rotary Motor – ATP Synthase



- Proton gradient drives F1 rotation accompanied by ATP synthesis from ADP.
- High ATP concentration drives rotation in opposite direction with ATP hydrolysis

(Reprinted with permission from Energy transduction in the F1 motor of ATP synthase, Wang , H. and G. Oster, <u>Nature</u>, 1998, **296**: 279-282. Permission Nature Publishing Group.)

Two functions of ATP synthase





https://youtu.be/nD9fyuisMkg

ATP synthase (video)





http://www.k2.phys.waseda.ac.jp/F1movies/F1Prop4C.gif

"Direct observation of the rotation of F₁-ATPase" Hiroyuki Noji, Ryohei Yasuda, Masasuke Yoshida, and Kazuhiko Kinosita, Jr. *Nature*, **386** (1997) 299-302.