

NANOPHYSIQUE

INTRODUCTION PHYSIQUE AUX NANOSCIENCES

2. PRINCIPALES METHODES DE MICROSCOPIE

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2023-2024

METHODES DE MICROSCOPIE

- **Paramètres Fondamentaux**
- **Microscopes Optiques**
 - **Principe**
 - **Améliorations:** phase contrast, dark field, fluorescent, ...
 - **Cristallographe aux Rayon X**
- **Microscope Electronique**
 - **à Transmission**
 - **à Balayage**
- **Microscope à emission champ**
- **Microscope à effet tunnel électronique**
- **Cryo-TEM**
- **Microscope à force atomique**
- **Optical Tweezers**
- **Light Scattering**

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MICROSCOPES OPTIQUES OU ELECTRONIQUES

Electromagnétisme (photons) ou mécanique quantique (électrons)

ONDES PROPAGATIVES:

$$\exp(ikx) = \exp(i2\pi x/\lambda)$$

Les ondes sont défléchies par les variations de l'indice de réfraction ou du potentiel perçu par les électrons.

Image obtenue dans la limite de courte longueur d'onde (optique géométrique ou mécanique classique)

$$\text{Diffraction limit : } d = \lambda/2n \sin\theta.$$

Résolution limitée par la longueur d'onde (diffraction):

Ondes électromagnétiques:

$$\lambda = c/v$$

$$c = 300000 \text{ km/s}$$

lumière visible: $\lambda = 500 \text{ nm}$

1000 X

rayons X: $\lambda = 0.1 - 10 \text{ nm}$

1000000 X

Ondes électroniques (de Broglie):

$$\lambda = h/p$$

$$h = 6.62 \cdot 10^{-34} \text{ J s}$$

impulsion après accélération dans un potentiel électrique V:

$$p = (2meV)^{1/2}$$

$$V = 40 - 1500 \text{ kV}$$

$$\lambda = 1 - 0.05 \text{ nm}$$

$$1000000 \text{ X} - 50000000 \text{ X}$$

ONDES EVANESCENTES: effet tunnel

$$\exp(-\kappa x) = \exp(-x/l)$$

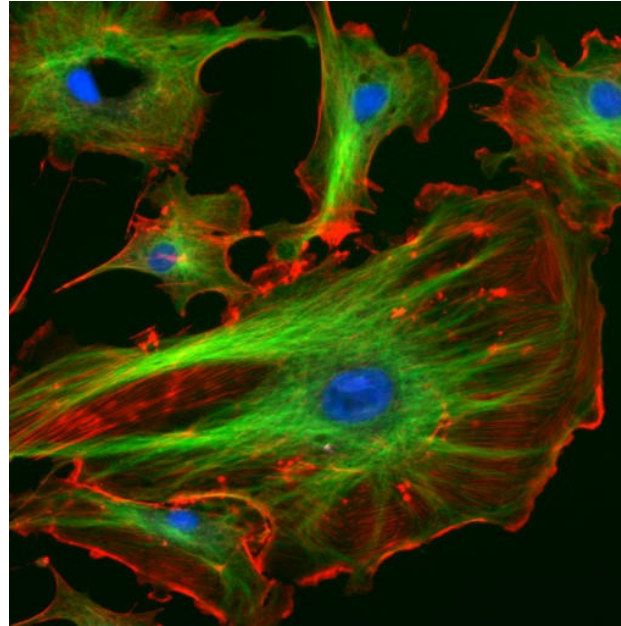
méthode local: balayage

MICROSCOPES OPTIQUES

lumière visible: $\lambda = 500 \text{ nm}$ 1000 X résolution latérale 200 nm

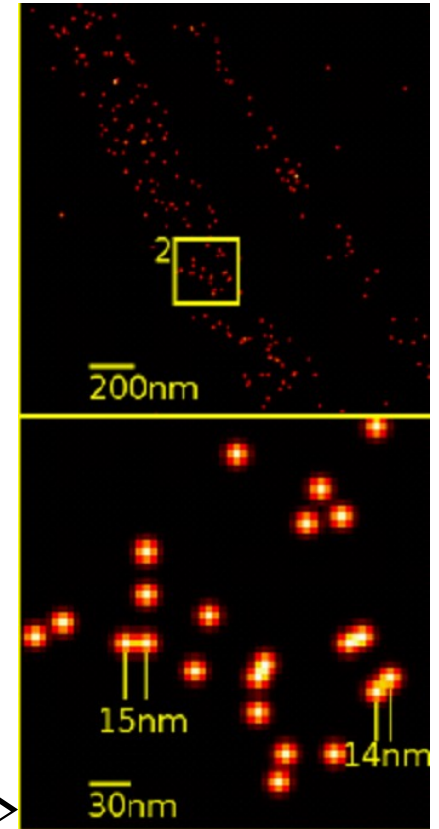
Méthodes sous-diffractives: résolution de 10 nm pour des objets quasi ponctuels

Microscope à fluorescence: molécules/protéines fluorescentes



Cellules endothéliales d'artères pulmonaires de bovins: \wedge
noyaux en bleu, microtubules en vert, filaments d'actine en rouge

Détection de molécules YFP individuelles dans des cellules de cancer humain \triangleright



Microscope confocal: balayage dans le plan focal: images 3D:
résolution latérale 160-180 nm résolution en profondeur 600 nm

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Techniques Optique

Microscope optique

Principe de base: faire passer la lumière visible transmise à travers ou réfléchi par l'échantillon à travers des lentilles simples ou multiples pour permettre une vue agrandie de l'échantillon.

Limitation: Résolution limitée par la longueur d'onde (diffraction) :
500nm (lumière visible) – 0.1nm (rayonne X)

Illumination: par réflexion ou transmission

Améliorations comprennent:

- Phase contrast
- Dark field
- Fluorescent
- Sous-diffraction
- Confocal

La limite de diffraction: “Scalar electrodynamics”

Motivation: All microscopes based on waves (visible lights, xrays, etc.) form images by collecting light via an aperature (e.g. a lens). The finite size of any lens causes distortions due to the borders of the lens. This ultimately gives rise to the diffraction limit.

Approach: Since wave phenomena are generic, we will study this effect using a simple model of waves called “scalar electrodynamics”.

First: we prove a useful theorem (tool) called the Kirkoff integral theorem.

Then: we use it to understand diffraction due to the finite size of an aperature.

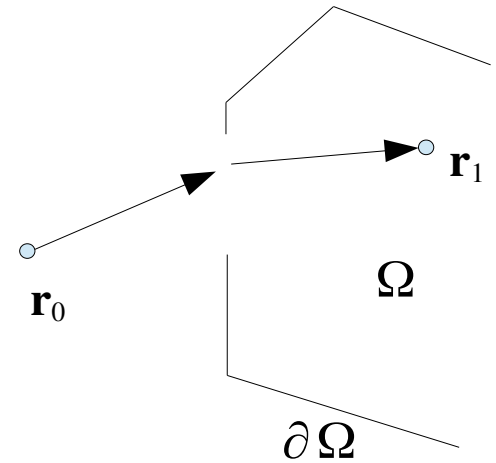
La limite de diffraction: Kirkoff integral theorem

Green's second identity:

$$\int_{\Omega} (U \nabla^2 V - V \nabla^2 U) d\mathbf{r} = \int_{\partial\Omega} (U \nabla V - V \nabla U) \cdot \hat{\mathbf{n}} dS$$

Si
$$c^2 \nabla^2 \begin{pmatrix} U \\ V \end{pmatrix} - \frac{\partial^2}{\partial t^2} \begin{pmatrix} U \\ V \end{pmatrix} = 0$$

et
$$\begin{aligned} U(\mathbf{r}; t) &= u(\mathbf{r}) e^{i\omega t} \\ V(\mathbf{r}; t) &= v(\mathbf{r}) e^{i\omega t} \end{aligned} \quad c^2 \nabla^2 \begin{pmatrix} u \\ v \end{pmatrix} - k^2 \begin{pmatrix} u \\ v \end{pmatrix} = 0, \quad k^2 = \omega^2 / c^2$$



on trouve que
$$\int_{\partial\Omega} (u \nabla v - v \nabla u) \cdot \hat{\mathbf{n}} dS = \int_{\Omega} (u \nabla^2 v - v \nabla^2 u) d\mathbf{r} = 0$$

En supposant que la volume est defini par deux surface: un grande surface (a "infini") et un petite sphere a rayon R avec centre \mathbf{r}_1 et si l'on choisit

$$v(\mathbf{r}) = e^{ik|\mathbf{r}-\mathbf{r}_1|} / |\mathbf{r}-\mathbf{r}_1|$$

on trouve
$$\lim_{R \rightarrow 0} u(\mathbf{r}_1) = \frac{1}{4\pi} \int_{\partial\Omega} \left(\frac{e^{ik|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} \nabla u(\mathbf{r}) - u(\mathbf{r}) \nabla \frac{e^{ik|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} \right) \cdot \hat{\mathbf{n}} dS$$

Diffraction of a point source by a circular aperture

Point source at \mathbf{r}_0

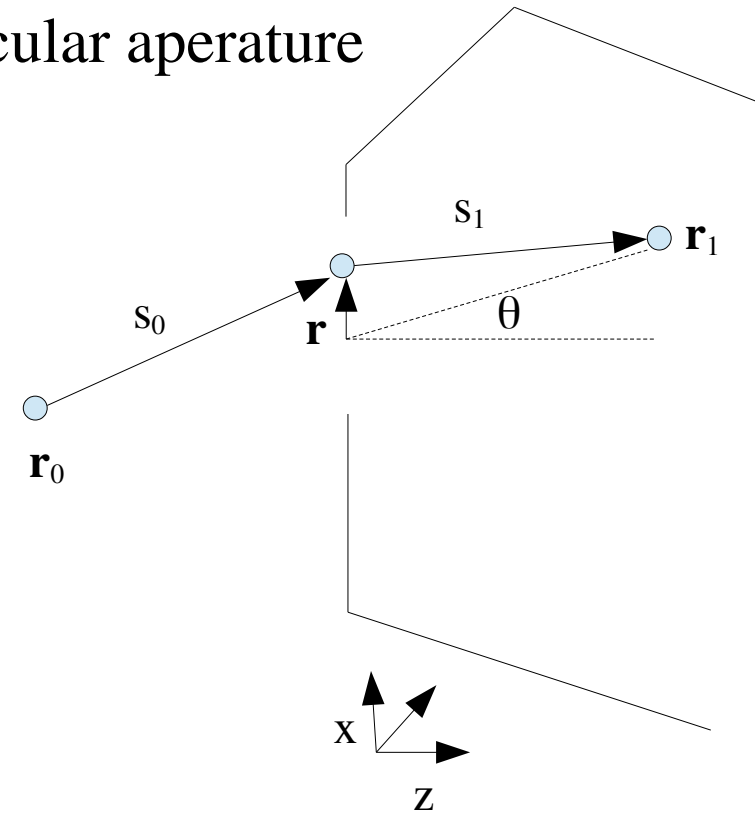
$$u(\mathbf{r}) = A \frac{e^{ik|\mathbf{r}-\mathbf{r}_0|}}{|\mathbf{r}-\mathbf{r}_0|}$$

Observe at point P at \mathbf{r}_1

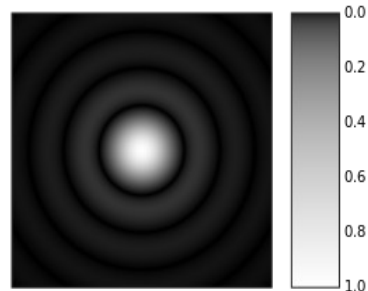
$$u(\mathbf{r}_1) = \frac{1}{4\pi} \int_{\partial\Omega} \left(\frac{e^{ik|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} \nabla u(\mathbf{r}) - u(\mathbf{r}) \nabla \frac{e^{ik|\mathbf{r}-\mathbf{r}_1|}}{|\mathbf{r}-\mathbf{r}_1|} \right) \cdot \hat{\mathbf{n}} dS$$

$$u(\mathbf{r}_1) = -\frac{iA}{2\lambda} \int_{\text{aperture}} \frac{e^{ik(s_0+s_1)}}{s_0+s_1} (\nabla s_0 - \nabla s_1) \cdot \hat{\mathbf{z}} dS$$

$$u(\mathbf{r}_1) = \frac{J_1(\pi D \sin \theta / \lambda)}{\pi D \sin \theta / \lambda}$$

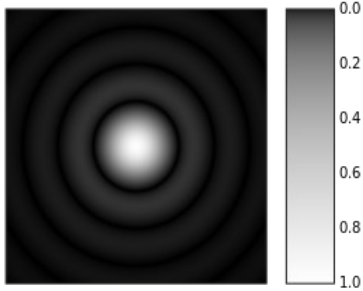


$D = \text{diameter}$

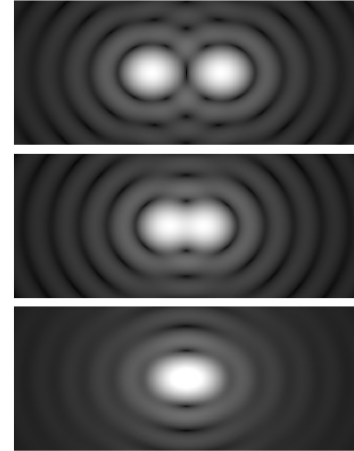


Airy disk

Diffraction limit



$$\theta = 1.22 \frac{\lambda}{D}$$



$$u(\mathbf{r}') = \frac{J_1(\pi D \sin \theta / \lambda)}{\pi D \sin \theta / \lambda}$$

Rayleigh criterion (max A = min B) $\Rightarrow \frac{\pi D \sin \theta}{\lambda} = 3.83.$

$$\Rightarrow \sin(\theta) = \left(\frac{1.22}{D} \right) \lambda$$

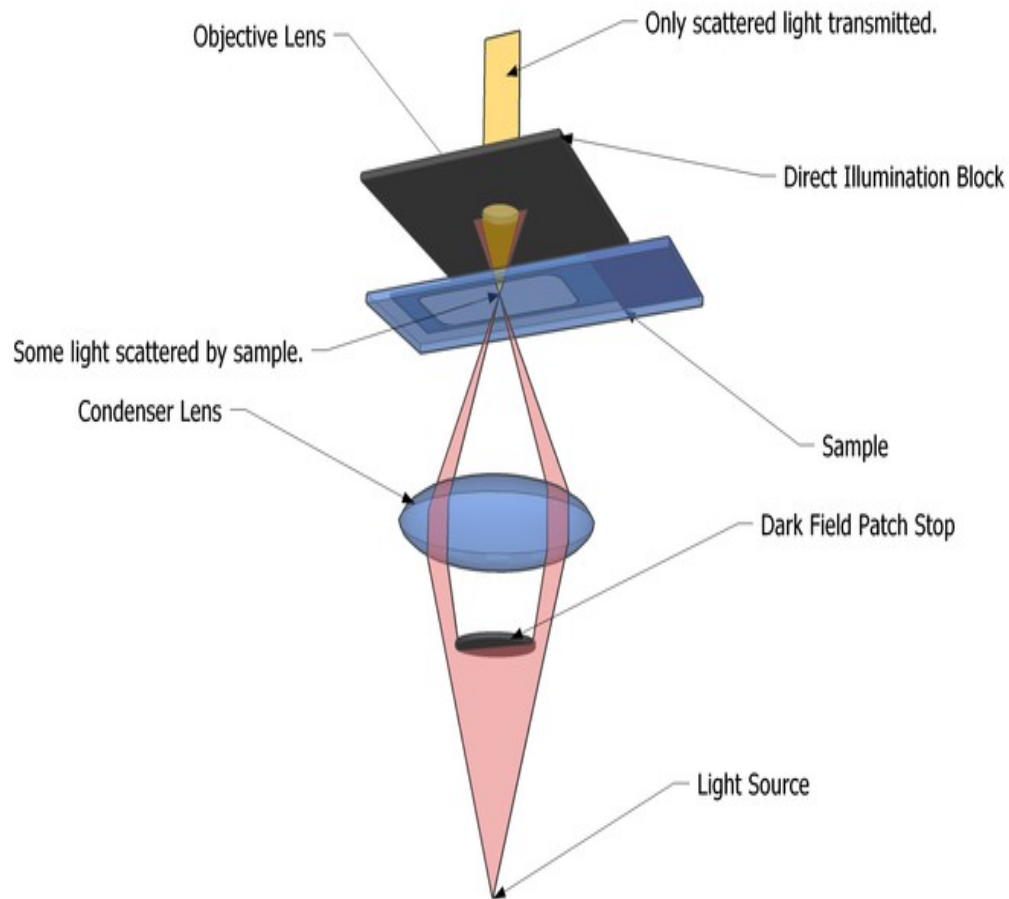
$$\Rightarrow \Delta l = f \sin(\theta) = \left(\frac{1.22 f}{D} \right) \lambda$$

Microscope optique

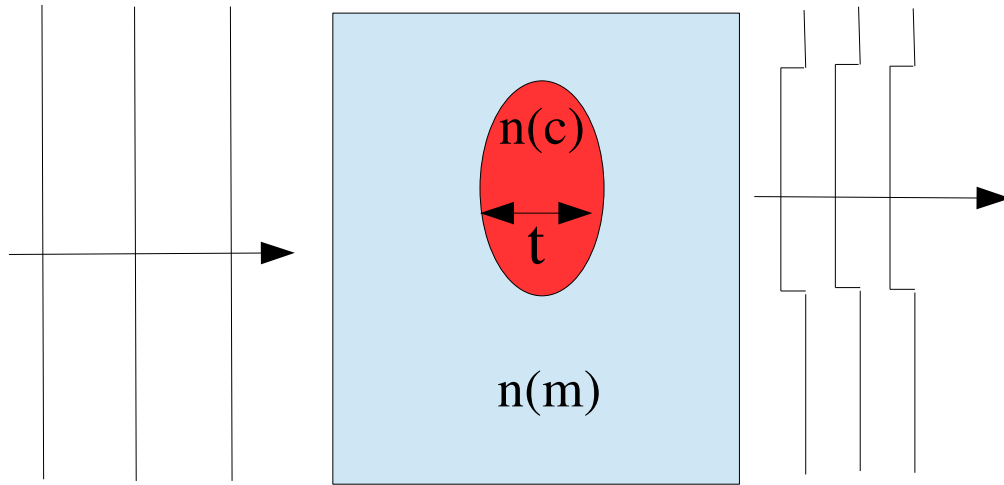
Le plus important technique pour améliorer le microscope optique est par **se diminuer ou éliminer tous la lumière** sauf ce qui pass a travers l'échantillon (ou, ce qui est diffusé par l'échantillon).

Champ Sombre (“Dark Field”)

L'idée: d'éliminer toute lumière sauf celle qui passe à travers l'échantillon.



Microscope optique “phase contrast”



$t \sim 5$ microns
 $n(\text{cell feature}) \sim 1.36$
 $n(\text{cell medium}) \sim 1.335$
 Optical path difference
 $= 5 \times (1.36 - 1.335)$
 $= 0.125$ microns
 $= 125 \text{ nm} = \frac{1}{4} \lambda$

Brightfield Microscopy Wave Phase Relationships

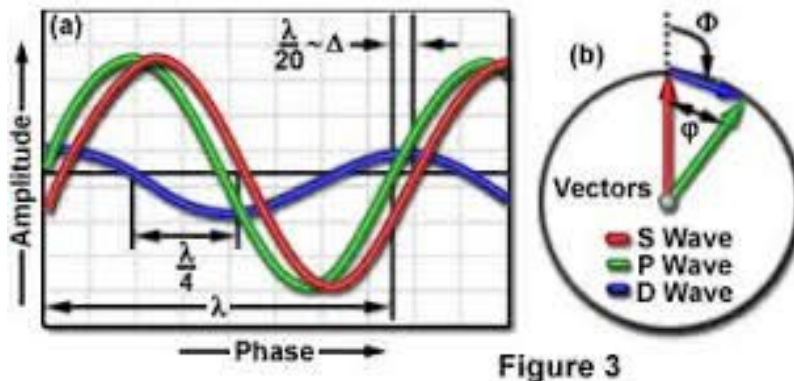


Figure 3

Positive and Negative Phase Contrast Systems

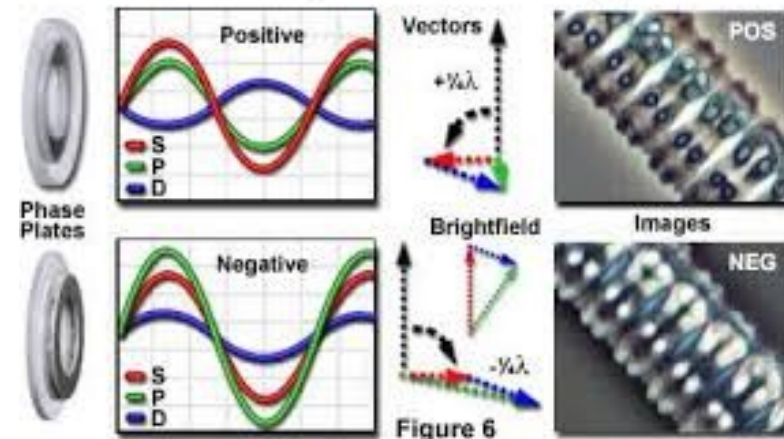
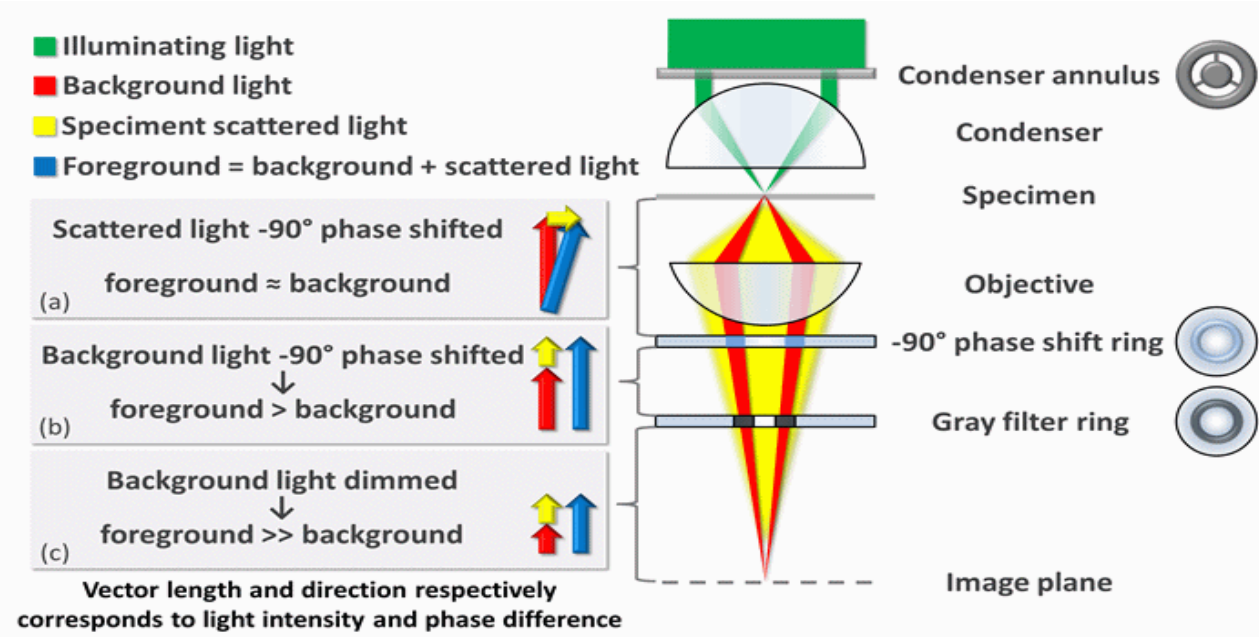


Figure 6

Microscope optique “phase contrast”

L'idée: pour les échantillons transparents, convertir la différence de phase des différences de l'amplitude.
Utilisé surtout pour l'imagerie biologique.



Principe de base:

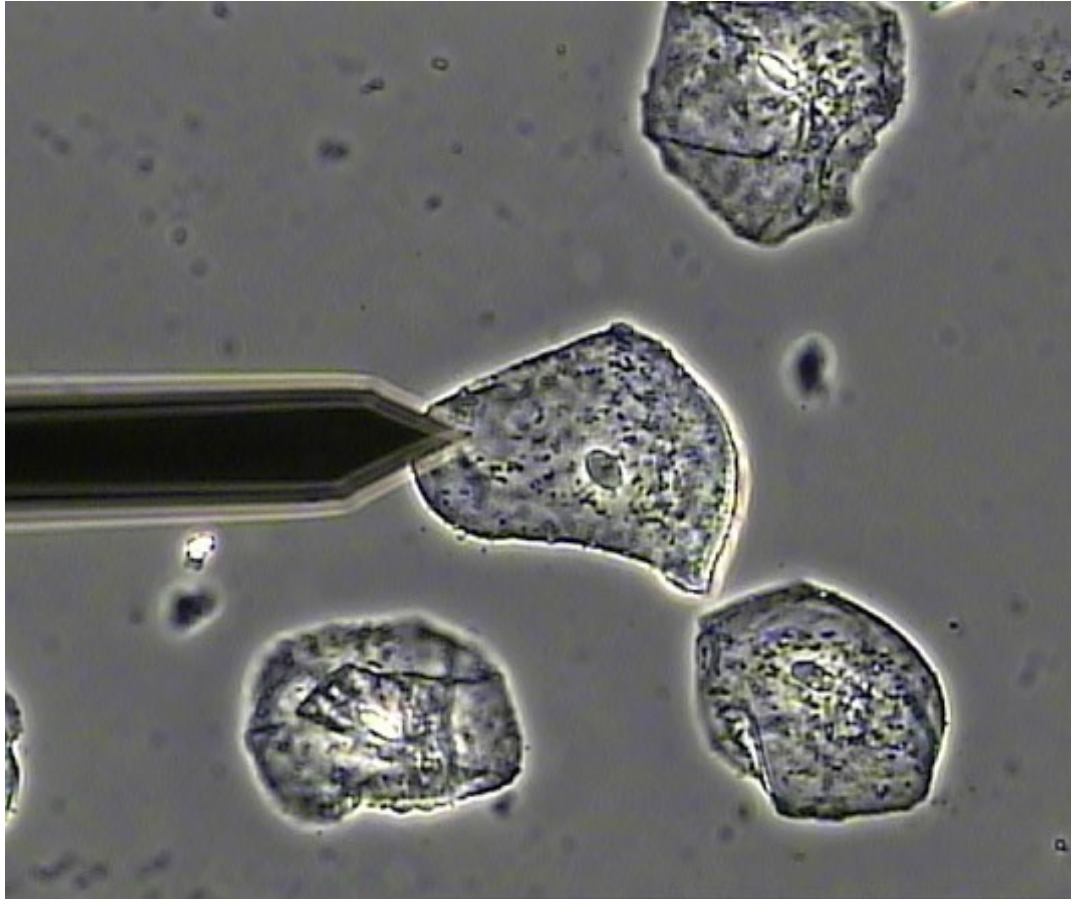
Il y a deux parcours optique:

Ce qui passe travers l'échantillon et ce qui pass librement.

- La premiere parcours provoque un changement de phase de 0 a $\frac{1}{4} \lambda$.
 - La deuxieme parcours passe par un “phase plate” qui provoque un changement de phase de $\frac{1}{4}$ et un “grey ring” qui diminue son amplitude.
- Résultat: une interférence constructive

Inventé par Frits Zernike
c. 1930 (Prix Nobel 1953).

Microscope optique “phase contrast”



Optical phase contrast of epithelial cells and AFM cantilever.

<http://www.asylumresearch.com/Gallery/BioScience/Optical/PhaseContrast/PhaseContrast!.jpg>

Microscope à fluorescence

Principe de base:

L'échantillon est tachée d'une substance fluorescente.

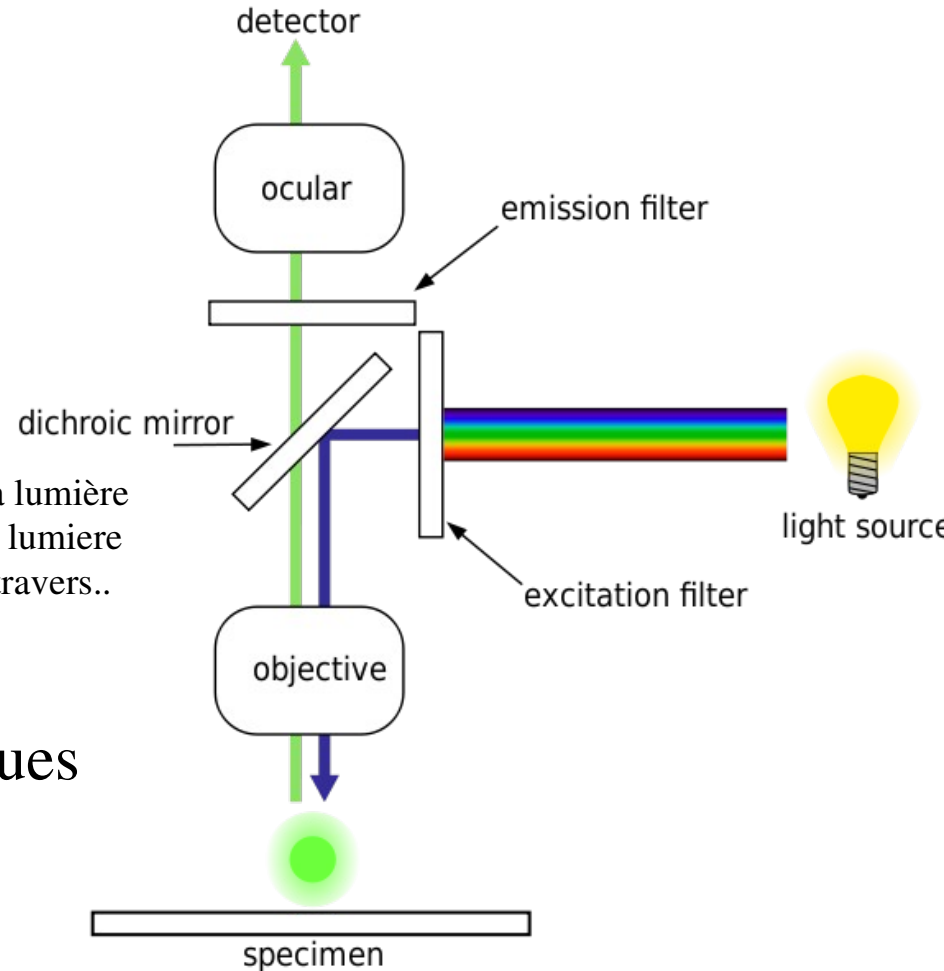
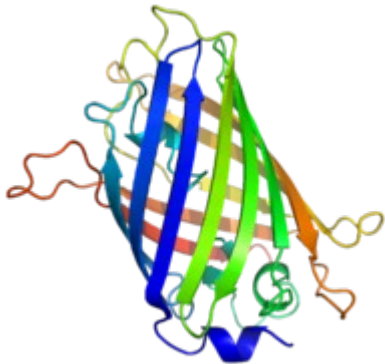
Utilisé surtout pour l'imagerie biologique.
Dans cet cas, on utilise souvent le “Green Fluorescent Protein” (GFP).

Miroir dichromatic: Elle réfléchit la lumière avec petite longueur d'onde mais la lumiere avec grand longueur d'onde passe à travers..

238 amino acid residues

~ 27 kDa

$\lambda = 395 \text{ nm}$

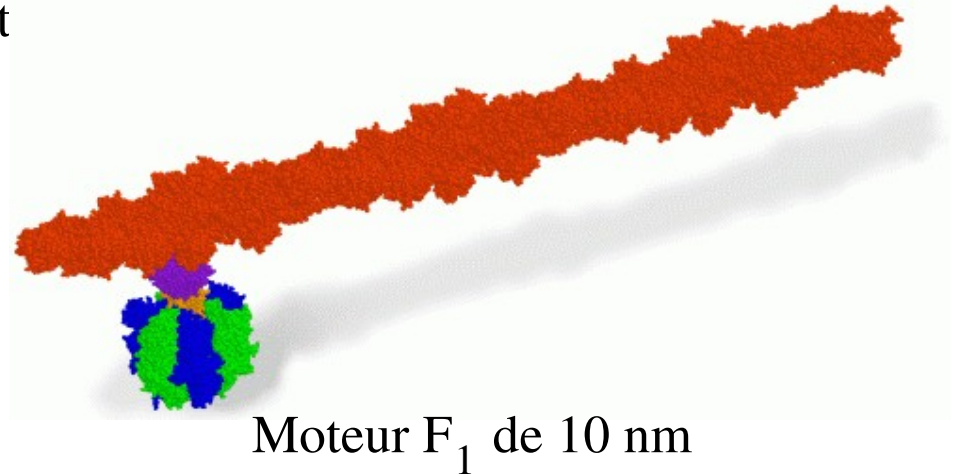


GFP découvert par Martin Chalfie, Osamu Shimomura, and Roger Y. Tsien 1960-1990
(Prix Nobel Chimie 2008).

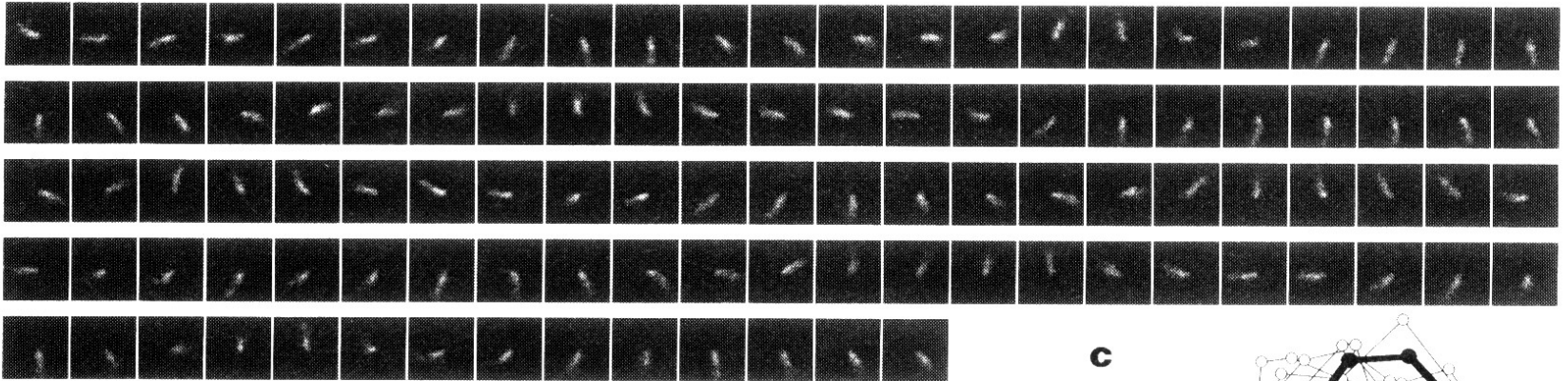
MICROSCOPE OPTIQUE A FLUORESCENCE

Possibilité d'observation du mouvement
dans des conditions ambiantes

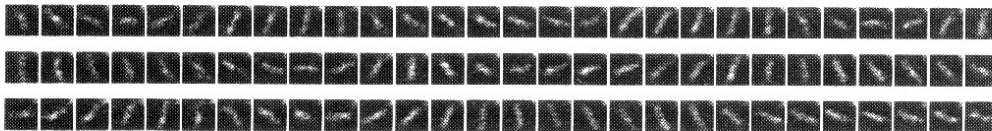
Filament d'actine de $1\mu\text{m}$
marqué par des molécules fluorescentes



a 0,5 tour / sec

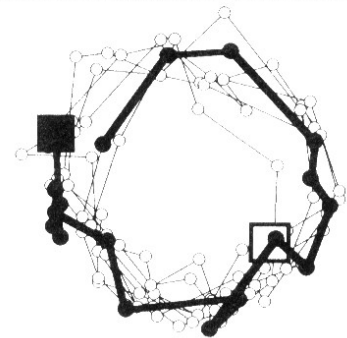


b 1,3 tour / sec

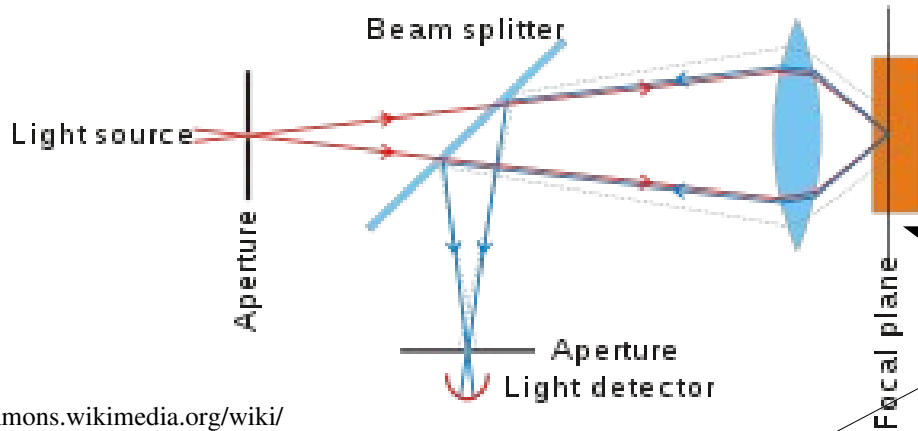


5 μm

c

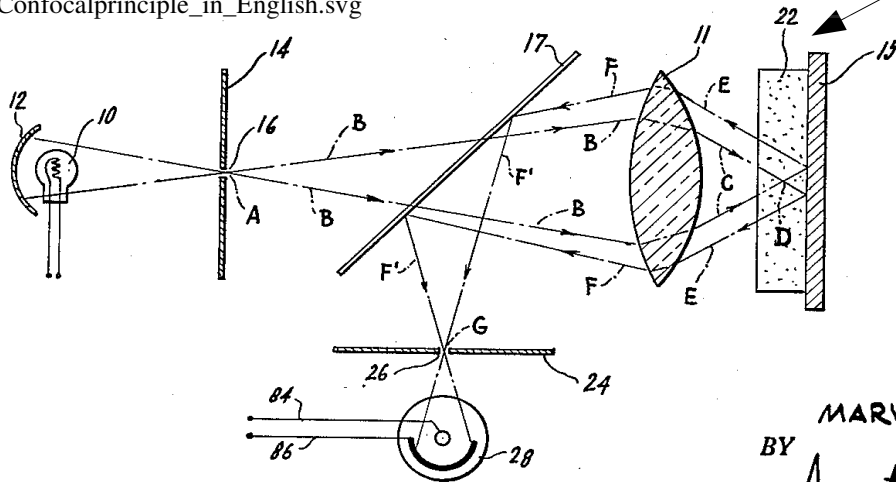


Confocal Microscopie



Lumière non focalisée contribue peu

https://commons.wikimedia.org/wiki/File:Confocalprinciple_in_English.svg



Résolution optimale d'environ
300x300x800 nm

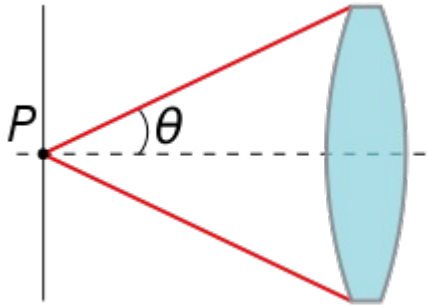
FIG. 3.

INVENTOR.
MARVIN MINSKY
BY *Ameter & Levy*
ATTORNEYS

From original patent of Marvin Minsky (1957).

En déplaçant le plan de mise au point permet d'obtenir une image en trois dimensions.

Sous-Diffraction



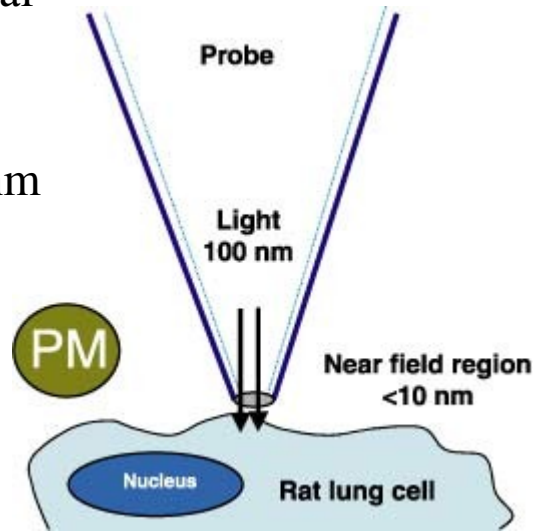
$$d = \lambda / 2n \sin\theta$$

Diffraction limit (Abbe 1873).

Near-field scanning optical microscope

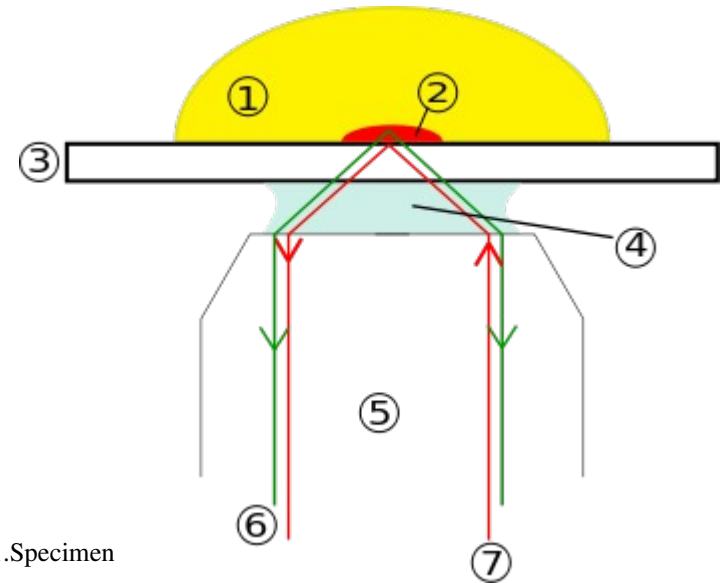
Resolution lateral: 20nm

Resolution vertical: 2-4 nm



<http://cals.arizona.edu/pubs/general/resrpt2001/13.html>

Total internal reflection fluorescence microscope (TIRFM)



1. Specimen
2. Evanescent wave range
3. Cover slip
4. Immersion oil
5. Objective
6. Emission beam (signal)
7. Excitation beam

<http://en.wikipedia.org/wiki/>

Total_internal_reflection_fluorescence_microscope

Sous-Diffraction

“Single-molecule localization microscopy”

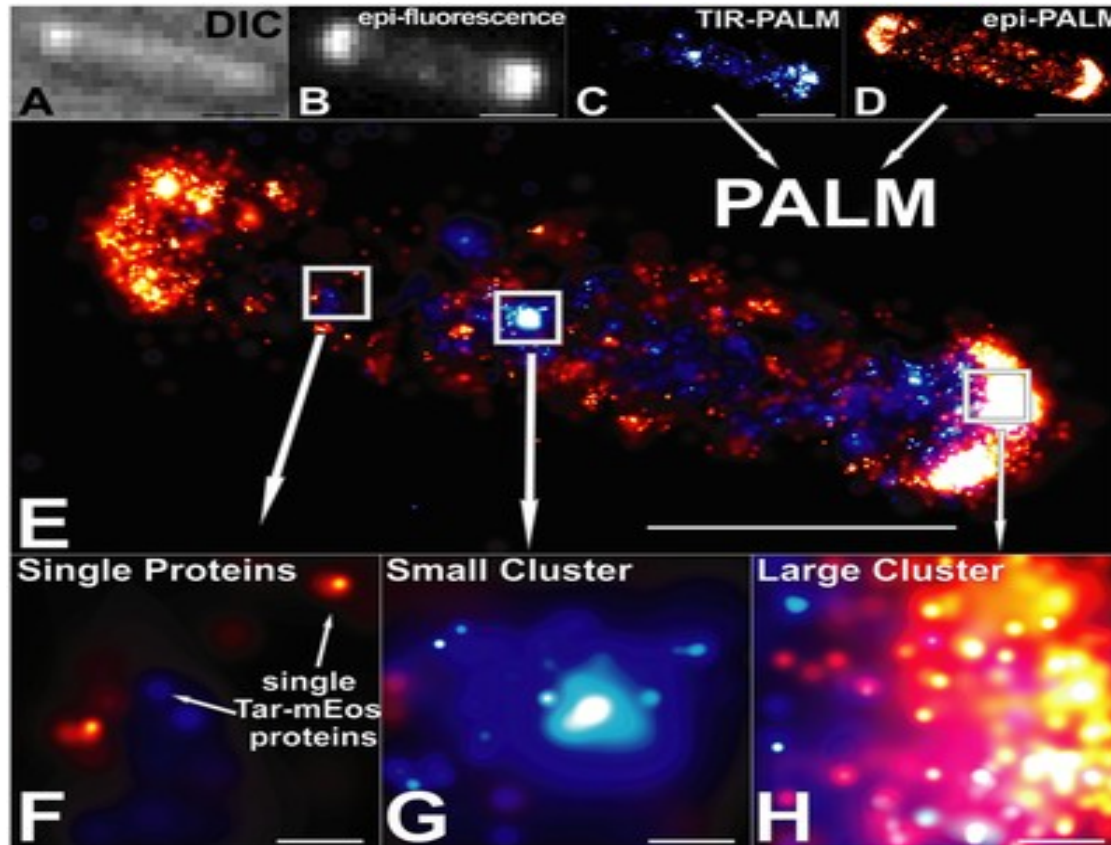
“Photo-activated localization microscopy (PALM)”

Airy disks



A sparse set of flourophores are activated at one time.
Position is center of Airy disk.
Further activation suppressed by “bleaching”.
Image built up over time.

Sous-Diffraction



Greenfield D, McEvoy AL, Shroff H, Crooks GE, Wingreen NS et al. (2009). "Self-Organization of the Escherichia coli Chemotaxis Network Imaged with Super-Resolution Light Microscopy." PLoS Biology 7 (6): e1000137. doi:10.1371/journal.pbio.1000137.

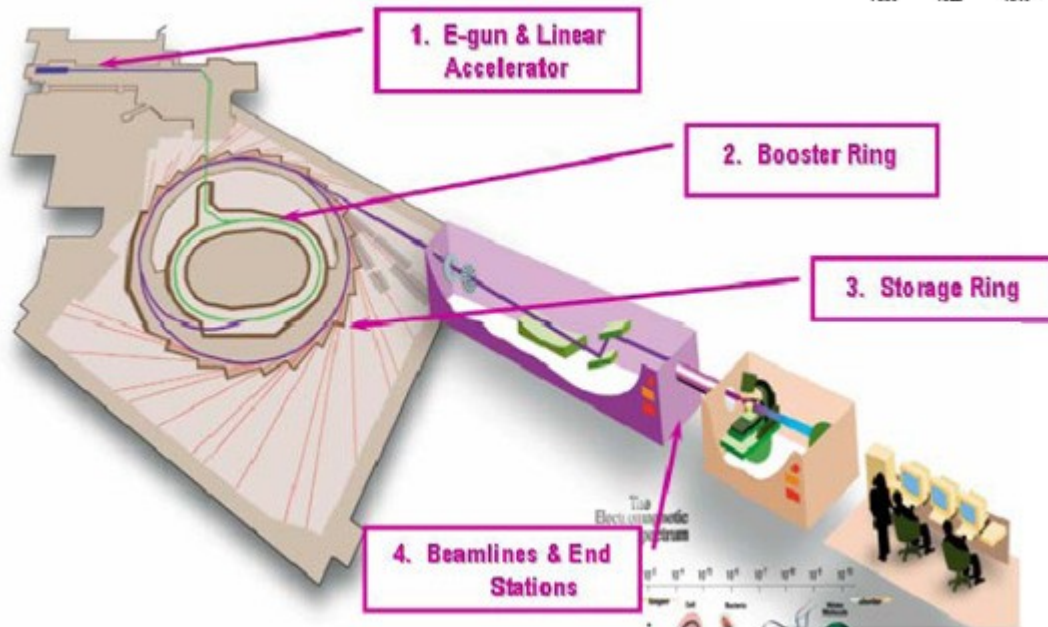
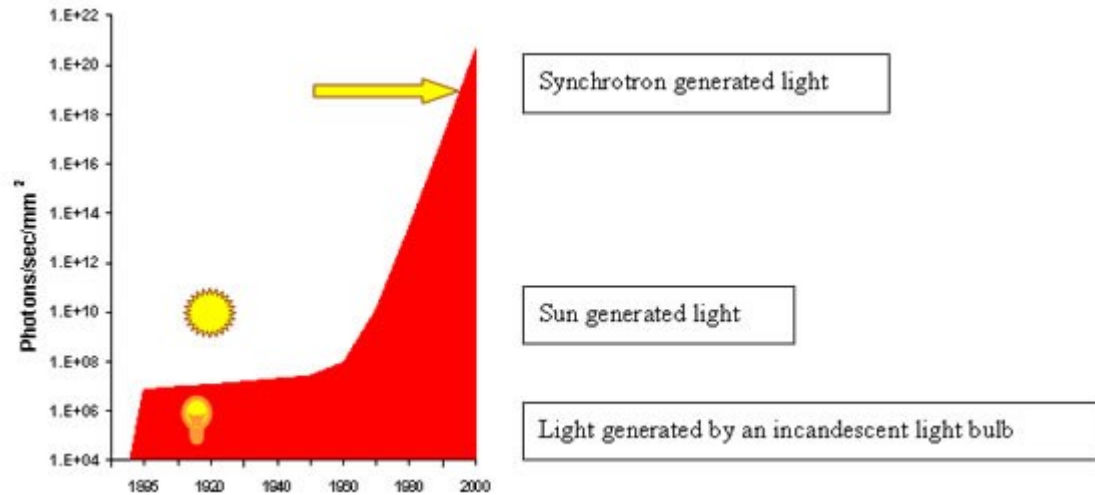
Figure 2. *E. coli* Δ tar cell with mEos-labeled Tar.

(A) Differential interference contrast (DIC) image of a single cell. (B) Diffraction-limited epi-fluorescence (epi). (C) PALM image in TIR-illumination. Each protein is represented as a 2-D Gaussian distribution whose width is the positional error for that protein. (D) PALM image in epi-illumination, taken after Tar-mEos proteins in the TIR region are bleached. (E) Superposition of (C) and (D). (F) Zoom of single proteins ($n = 44$ Tar proteins) in left boxed region of (E). (G) Zoom of small cluster ($n = 241$ Tar proteins) in middle boxed region of (E). (H) Zoom of large polar cluster ($n = 722$ Tar proteins) in right boxed region in (E). Scale bar in (A–E) indicates $1 \mu\text{m}$. Scale bar in (F–H) indicates 50 nm .

Synchrotron

Advantages:

- Intensité
- "In situ"
- Grand flux IR-Rayons X
- Vitesse



Credit: Canadian Light Source
<http://www.lightsource.ca/>

CRISTALLOGRAPHIE AUX RAYONS X

rayons X: $\lambda = 0.1 - 10 \text{ nm}$ 1000000 X

espacements des atomes ou des molécules dans les cristaux

synchrotrons

1912 CuSO_4 sulfate de cuivre *Max von Laue*

1914 NaCl (liaisons ioniques)

Diamant (C-C = 0.152 nm)

Cu

CaF_2 fluorite *W. L. Bragg*

CaCO_3 calcite

FeS_2 pyrite

- MgAl_2O_4 spinel

1916 TiO_2 (rutile & anatase)

graphite

...

1937 cholestérol *D. Cr. Hodgkin*

1945 vitamine B12 *D. Cr. Hodgkin*

1953 ADN *R. Franklin, M. Wilkins, J. D. Watson, F. Crick*

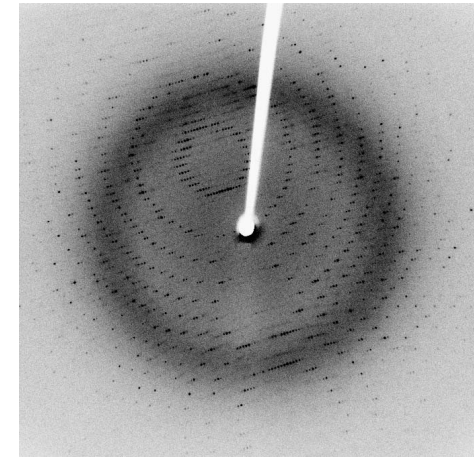
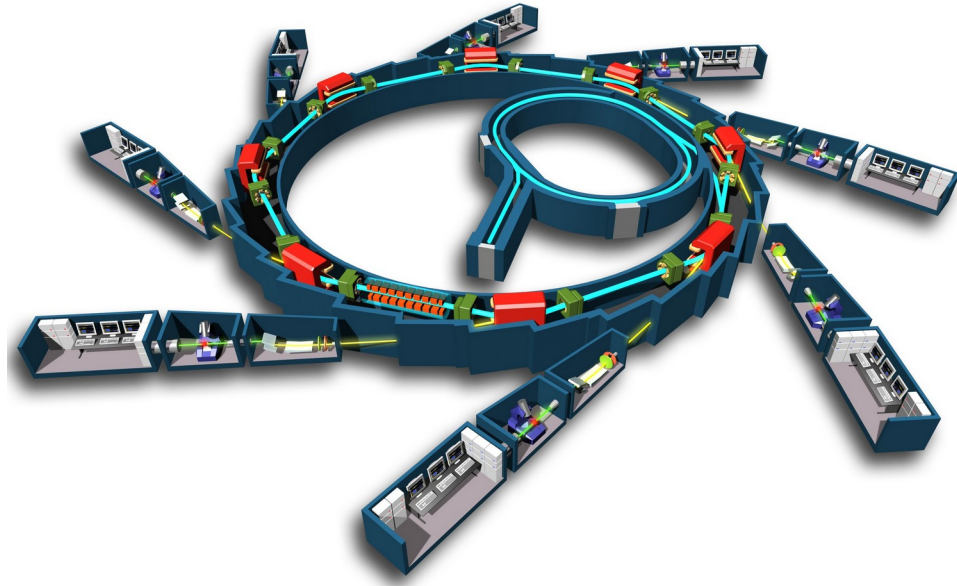
1954 pénicilline *D. Cr. Hodgkin*

1958 myoglobine *M. Perutz, J. C. Kendrew*

1969 insuline *D. Cr. Hodgkin*

1994 F_1 -ATPase *J. E. Walker et al.*

2000 ribosome *V. Ramakrishnan, T. A. Steitz, A. E. Yonath*



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MICROSCOPE ELECTRONIQUE A TRANSMISSION - TEM

Ondes électroniques (de Broglie):

$$\lambda = h/p$$

$$h = 6.62 \cdot 10^{-34} \text{ J s}$$

impulsion après accélération dans un potentiel électrique V :

$$p = (2meV)^{1/2}$$

$$V = 40 - 1500 \text{ kV}$$

$$\lambda = 1 - 0.05 \text{ nm}$$

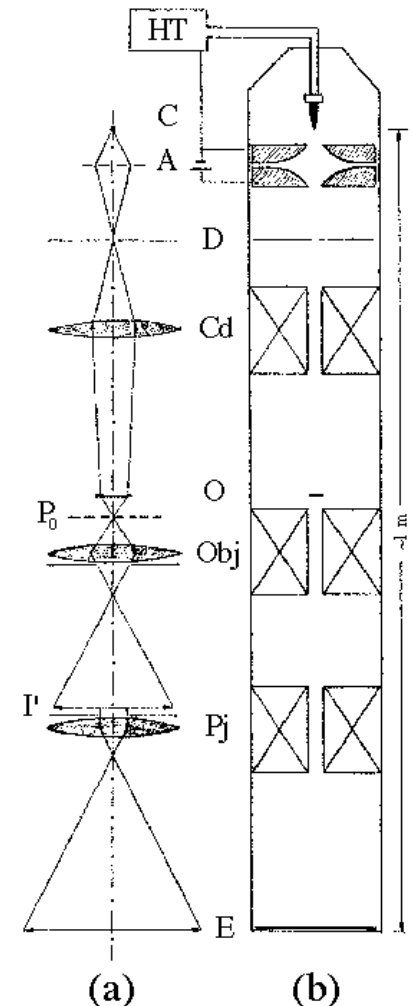
$$1000000 \text{ X} - 50000000 \text{ X}$$

1933 E. Ruska

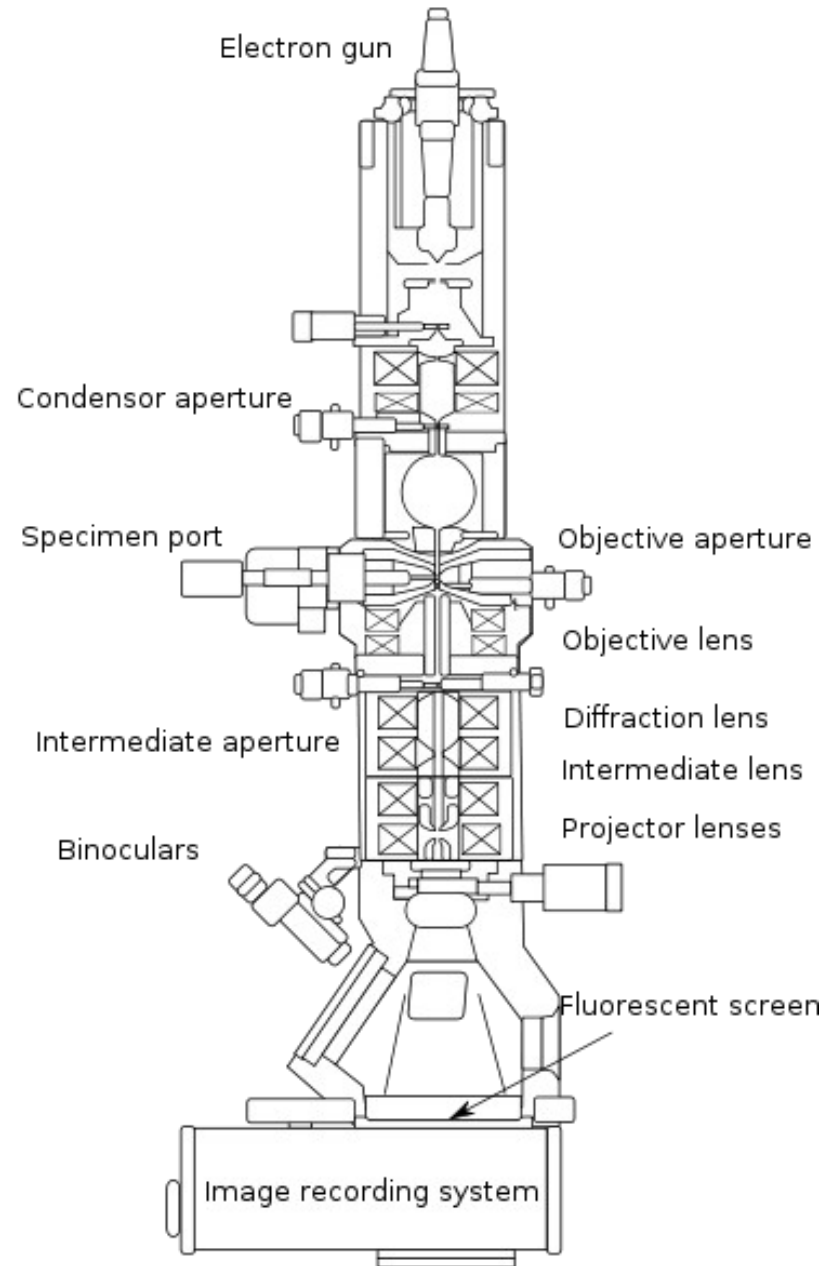
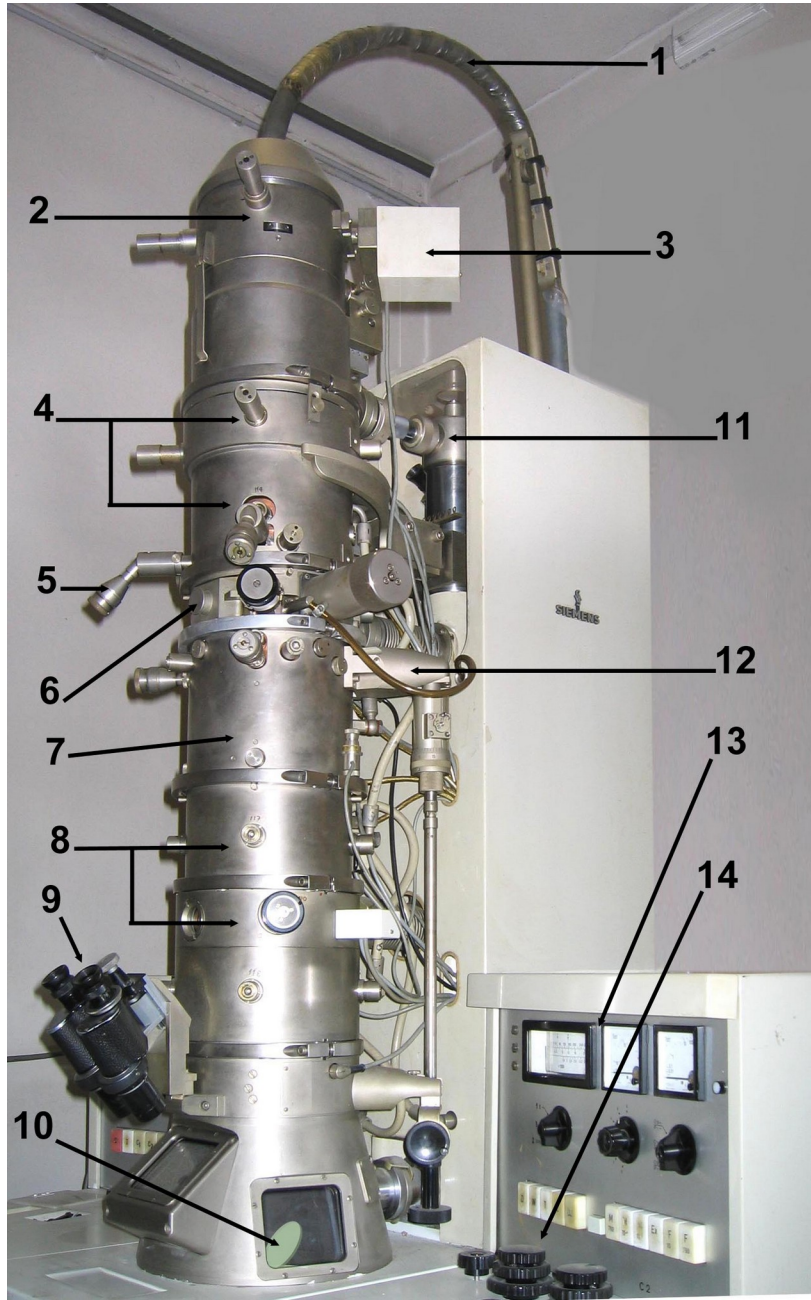
faisceau électronique dans le vide



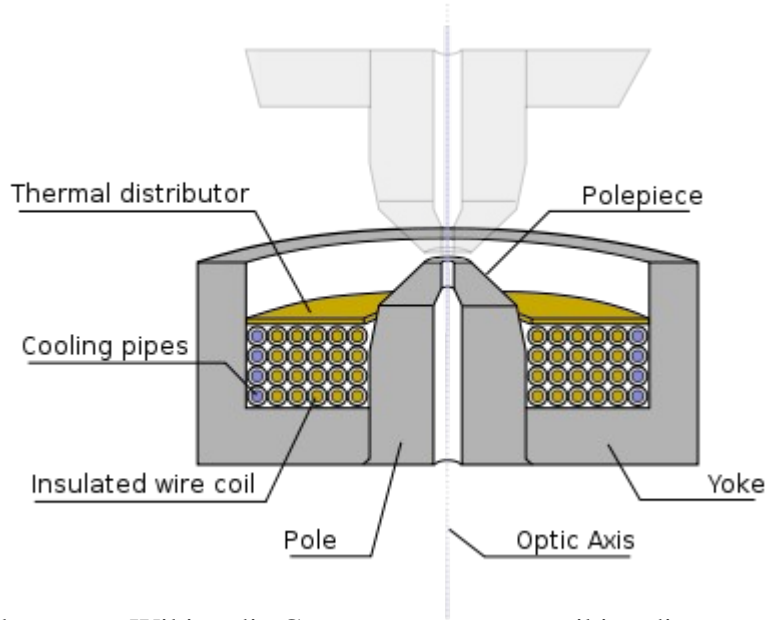
- HT alimentation haute tension
- du canon à électrons
- C cathode à émission de champ
- A anode double
- D diaphragme
- Cd lentille condensatrice
- O objet étudié
- P_0 plan de focalisation optimale
- Obj lentille objectif
- I' image intermédiaire
- P_j lentille projectrice
- E écran d'observation



MICROSCOPE ELECTRONIQUE A TRANSMISSION - TEM



MICROSCOPE ELECTRONIQUE A TRANSMISSION - TEM



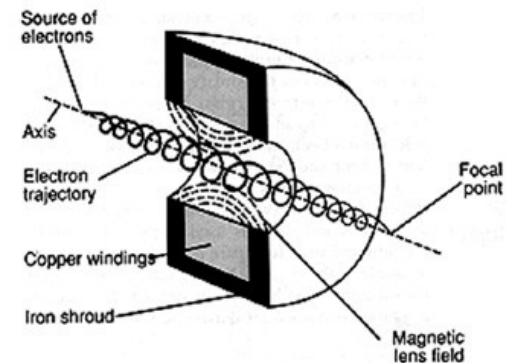
File:TEM-lens.svg - Wikimedia Commons commons.wikimedia.org



www.ammrf.org.au

Electromagnetic Lenses

Electromagnetic lenses are comprised of windings of wire through which electric current is applied. This creates a strong magnetic field through which negatively-charged electrons must pass.



Due to the magnetic field, the electrons follow a helical trajectory which converges at a fine focal point after it emerges from the lens. (DC-powered magnets behave similar to converging glass lenses)

Field Strength -determines the focal length which varies with:

$$(\text{focal length}) f = K (V / i^2)$$

K = constant based on the number of turns of lens coil wire and the geometry of the lens.

V = accelerating voltage

i = milliamps of current put through the coil

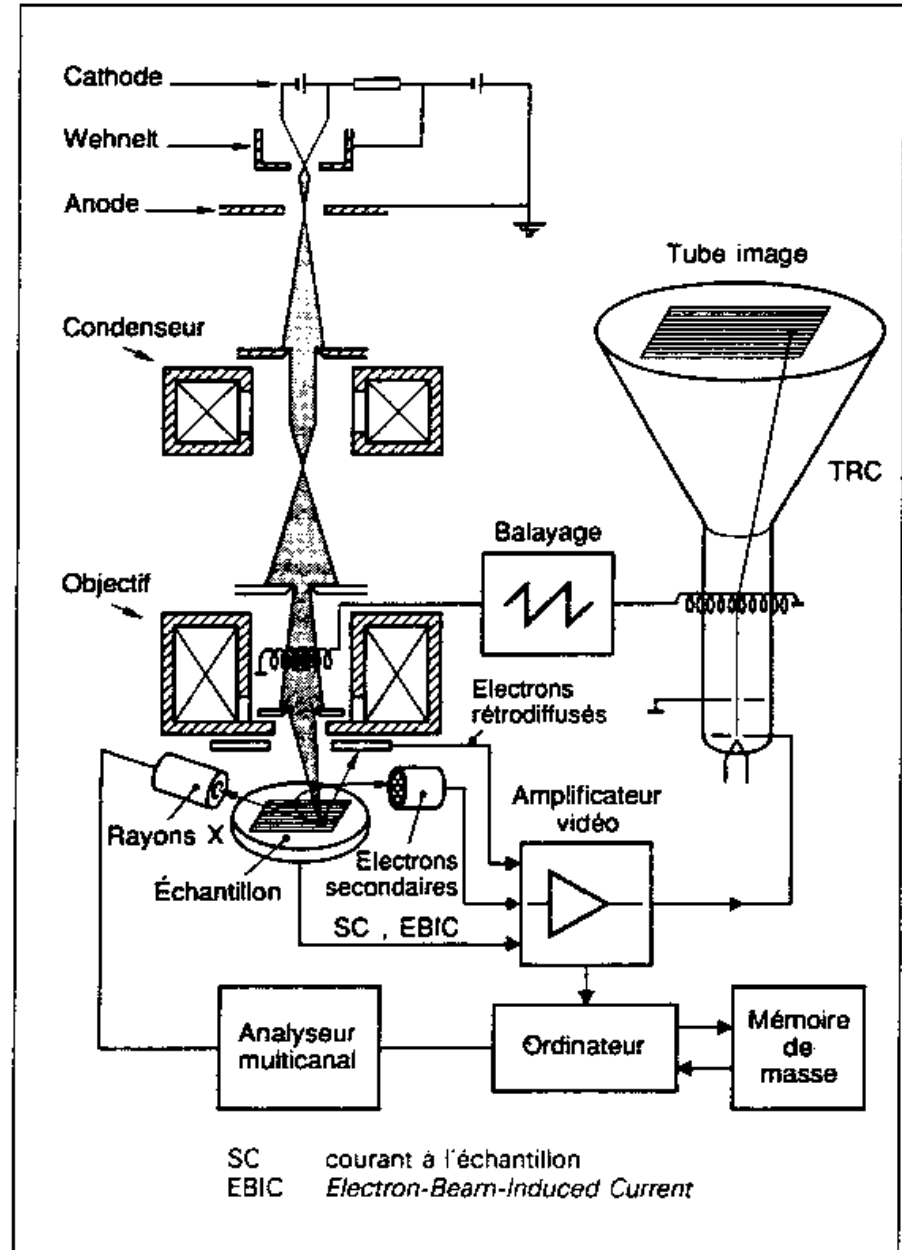
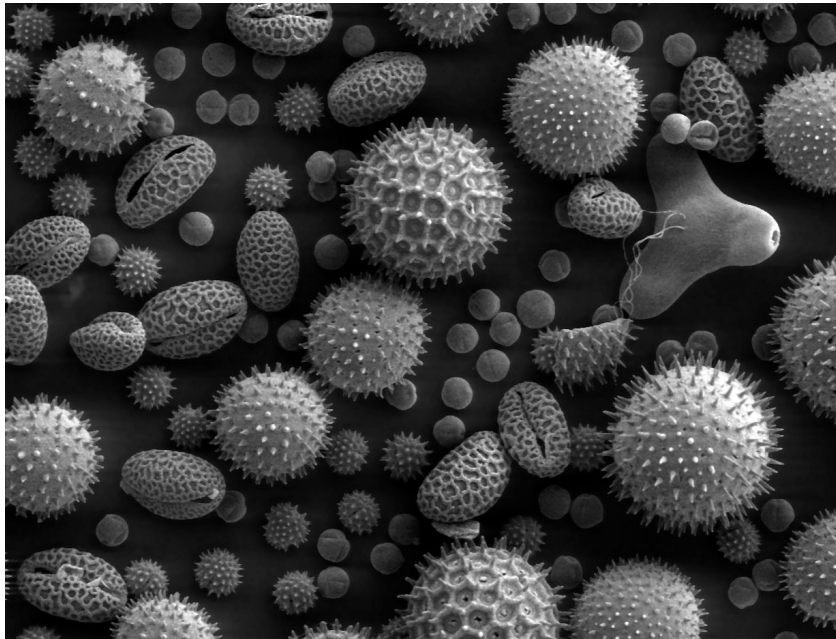
Potentiometer controls which vary the current to the various lenses are the means by which focus and magnification of the electron beam are achieved.

<http://www.udel.edu/biology/Wags/b617/tem/tem6.gif>

MICROSCOPE ELECTRONIQUE A BALAYAGE - SEM

- faisceau dans le vide
- couche métallique sur l'échantillon

grains de pollen (micromètres)



SEM + MICROANALYSEUR A RAYONS X

Spectrographe à rayons X:
analyse chimique in situ

Niveaux électroniques du cœur atomique

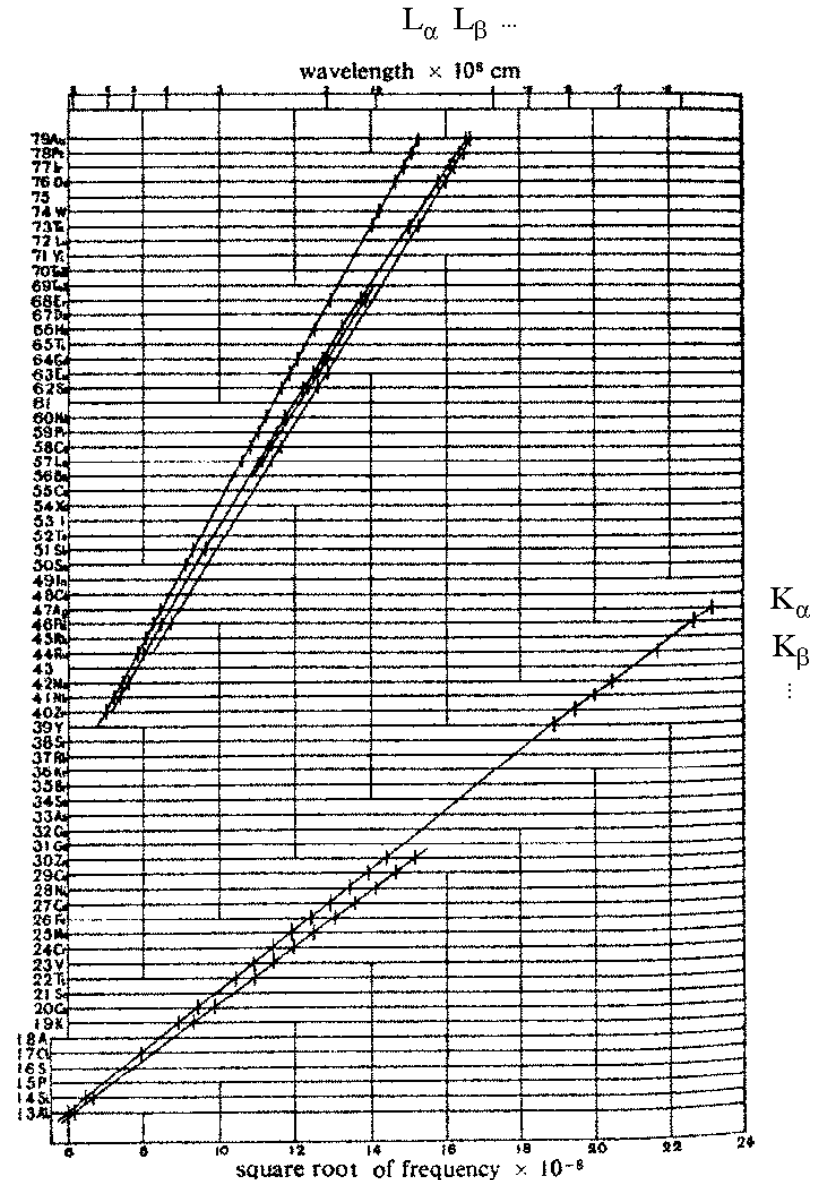
Modèle de Bohr:

$$E_n = -13.6 \text{ eV } Z^2/n^2$$

$$h \nu = E_m - E_n$$

Loi de Moseley:

$$Z = Z_e + a \nu^{1/2}$$



METHODES DE MICROSCOPIE

- Paramètres Fondamentaux
- Microscopes Optiques
 - Principe
 - Améliorations: phase contrast, dark field, fluorescent, ...
 - Cristallographe aux Rayon X
- Microscope Electronique
 - à Transmission
 - à Balayage
- **Microscope à emission champ**
- Microscope à effet tunnel électronique
- Cryo-TEM
- Microscope à force atomique
- Optical Tweezers
- Light Scattering

MICROSCOPE A EMISSION DE CHAMP

E. W. Müller (1951-1955)

FEM: « Field emission electron microscope » (FEEM)
Electrons émis par une pointe à un potentiel négatif
(pas de résolution atomique)

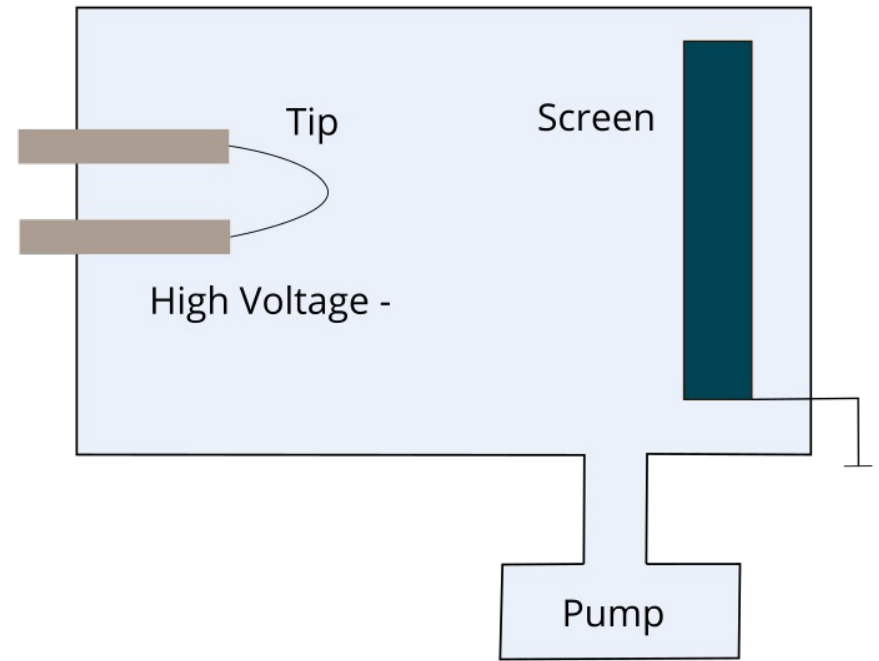
FIM: « Field ion microscope »
Pointe à un potentiel positif:
gaz révélateur dans l'enceinte (néon)
dont les atomes s'ionisent sur la pointe et sont projetés sur l'écran
(résolution atomique dans les conditions cryogéniques 50 K)
(résolution atomique perdue à plus hautes températures)

$$r = 10 - 100 \text{ nm} \quad \rightarrow \quad R = 10 \text{ cm}$$

Microscope à émission de champ

E. W. Müller (1951-1955)

Explosion coulombienne
par effet de pointe sous une
forte différence de potentiel
électrique

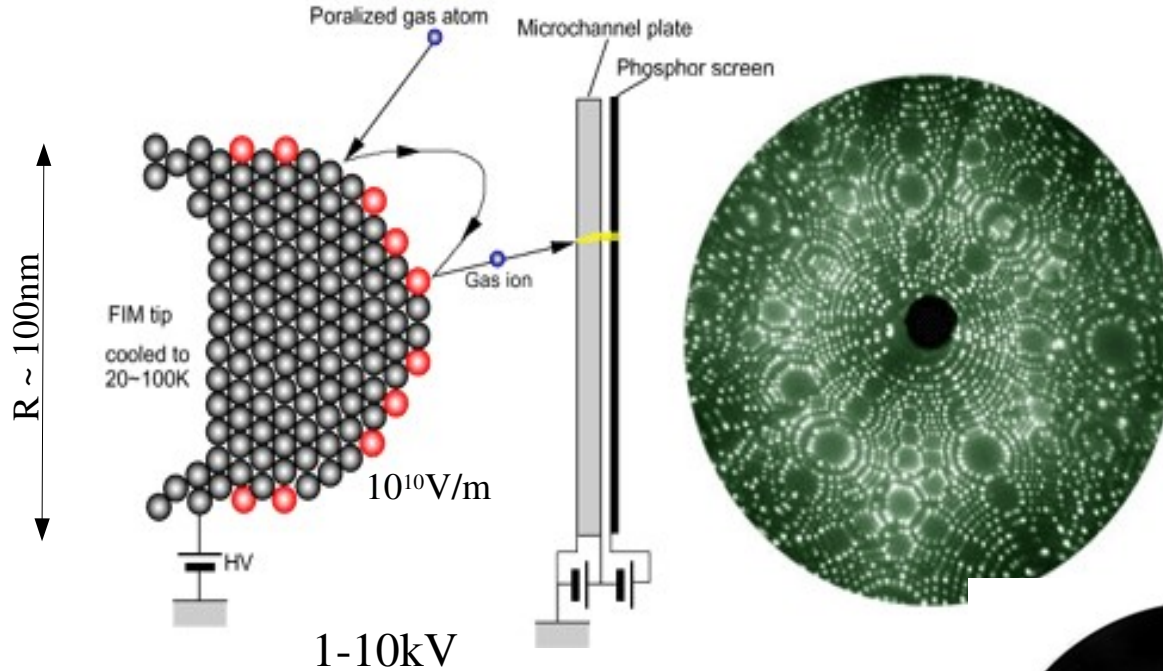


Wikipedia

1-10kV potentiel difference

1-2nm resolution

FIM



“la première méthode pour visualiser les atomes”

magnification = L/R

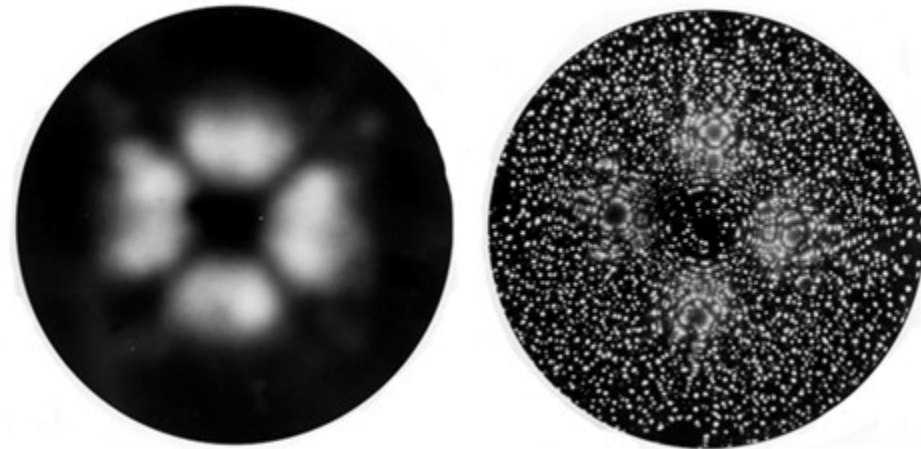


Fig. 2 FEM and FIM images of a clean Ni surface. Both images were obtained from the identical surface of a Ni tip. (Curtsy of K. Hono, NRIM)

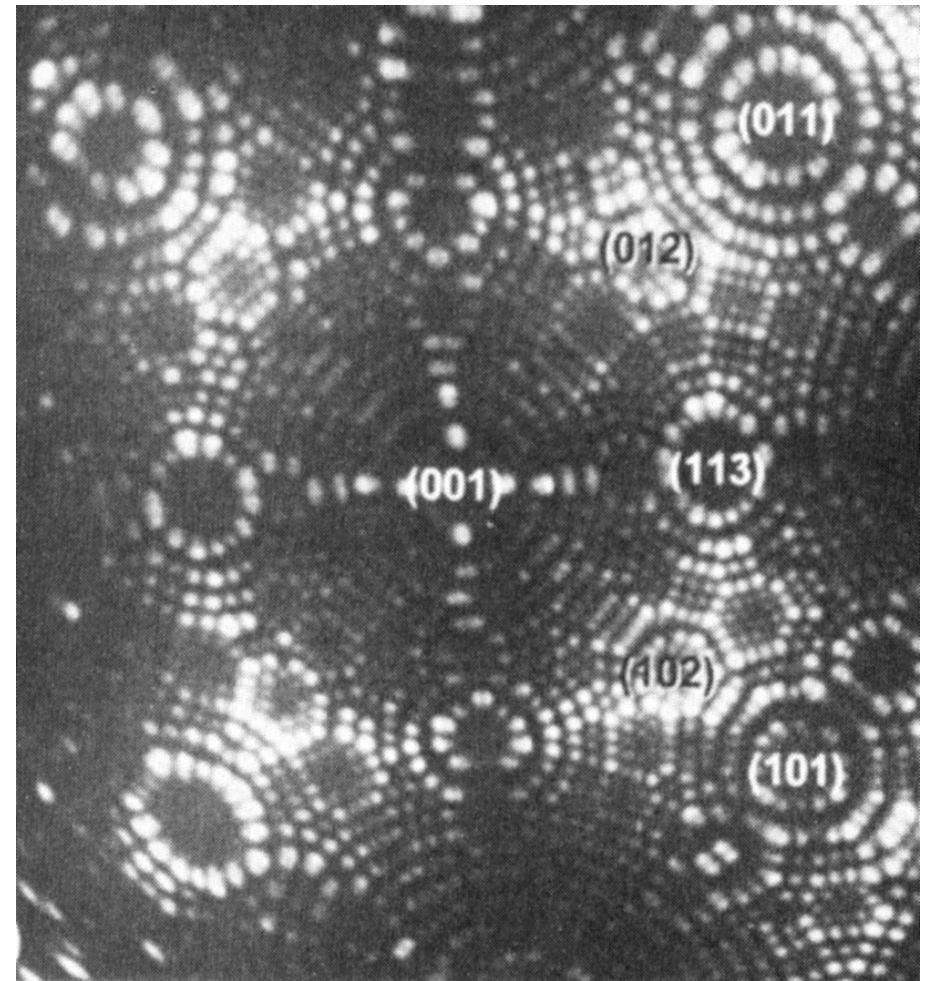
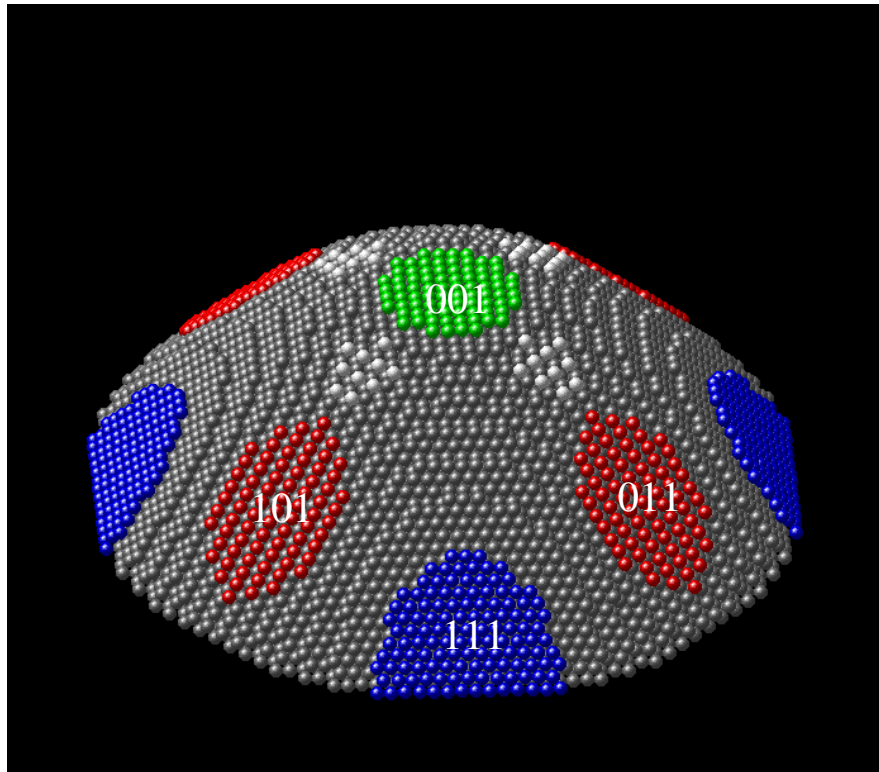
Microscope à émission de champ

Laboratoire de Norbert Kruse, ULB

Pointe de platine (diamètre ~20 nm)

gaz révélateur: néon

champ électrique: 35 V/nm



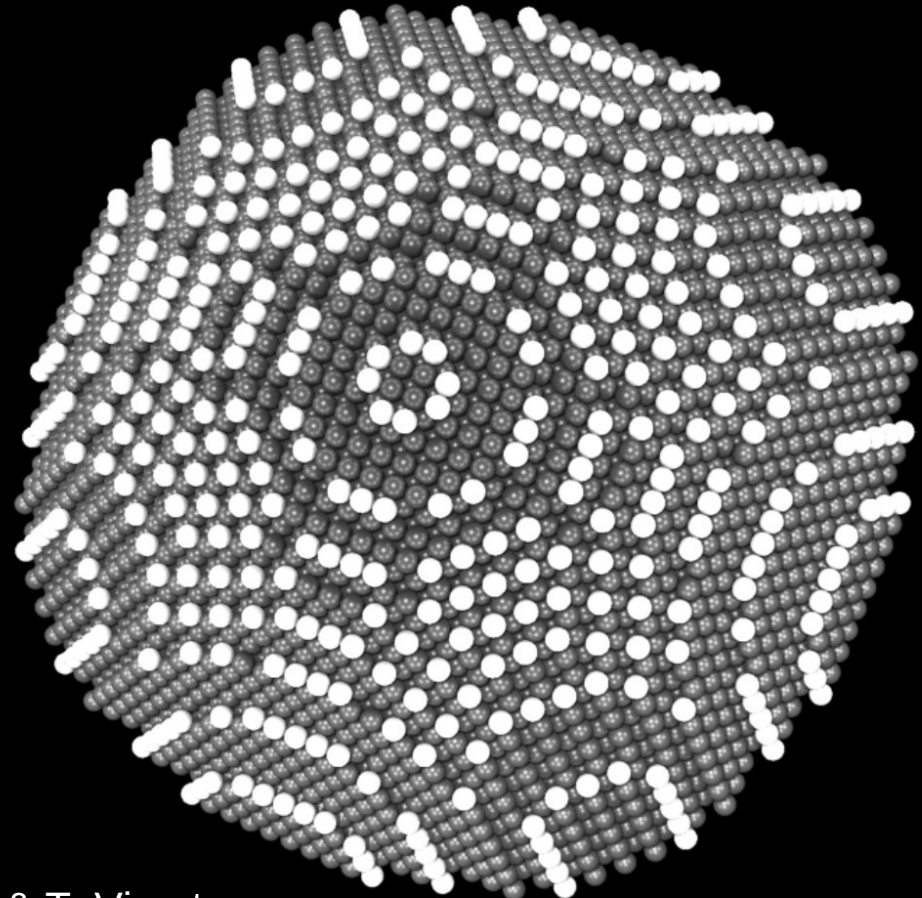
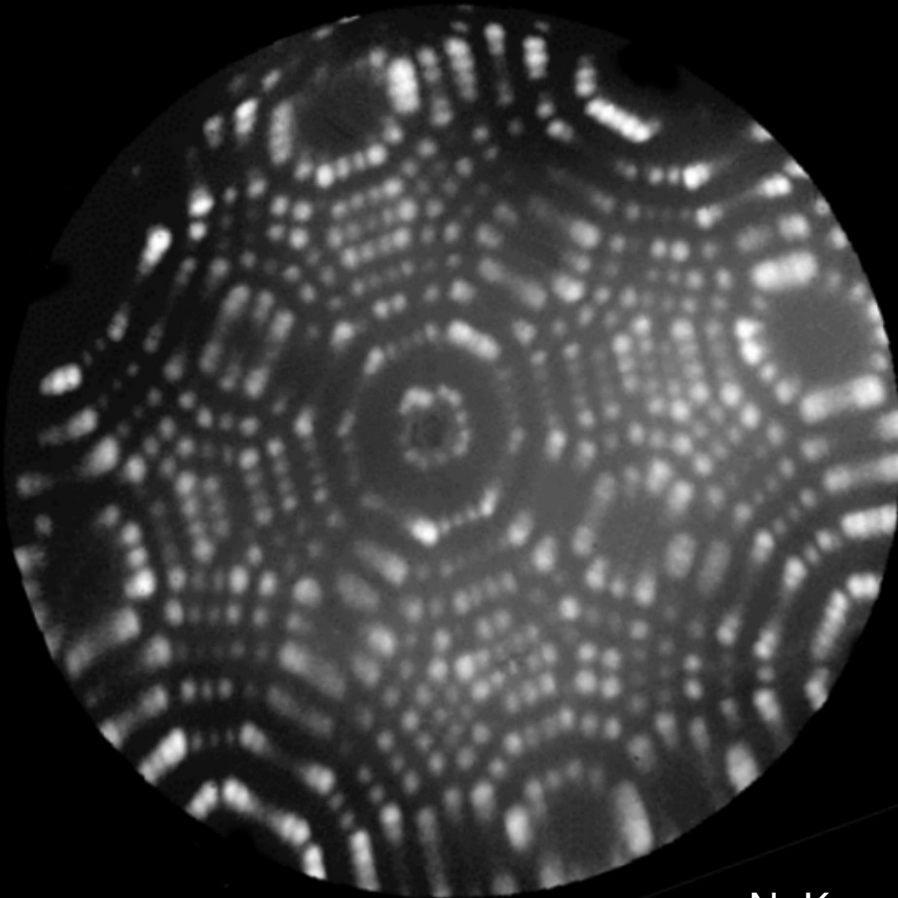
Microscope à émission de champ

Laboratoire de Norbert Kruse, ULB

pointe de rhodium (diamètre ~10 nm)

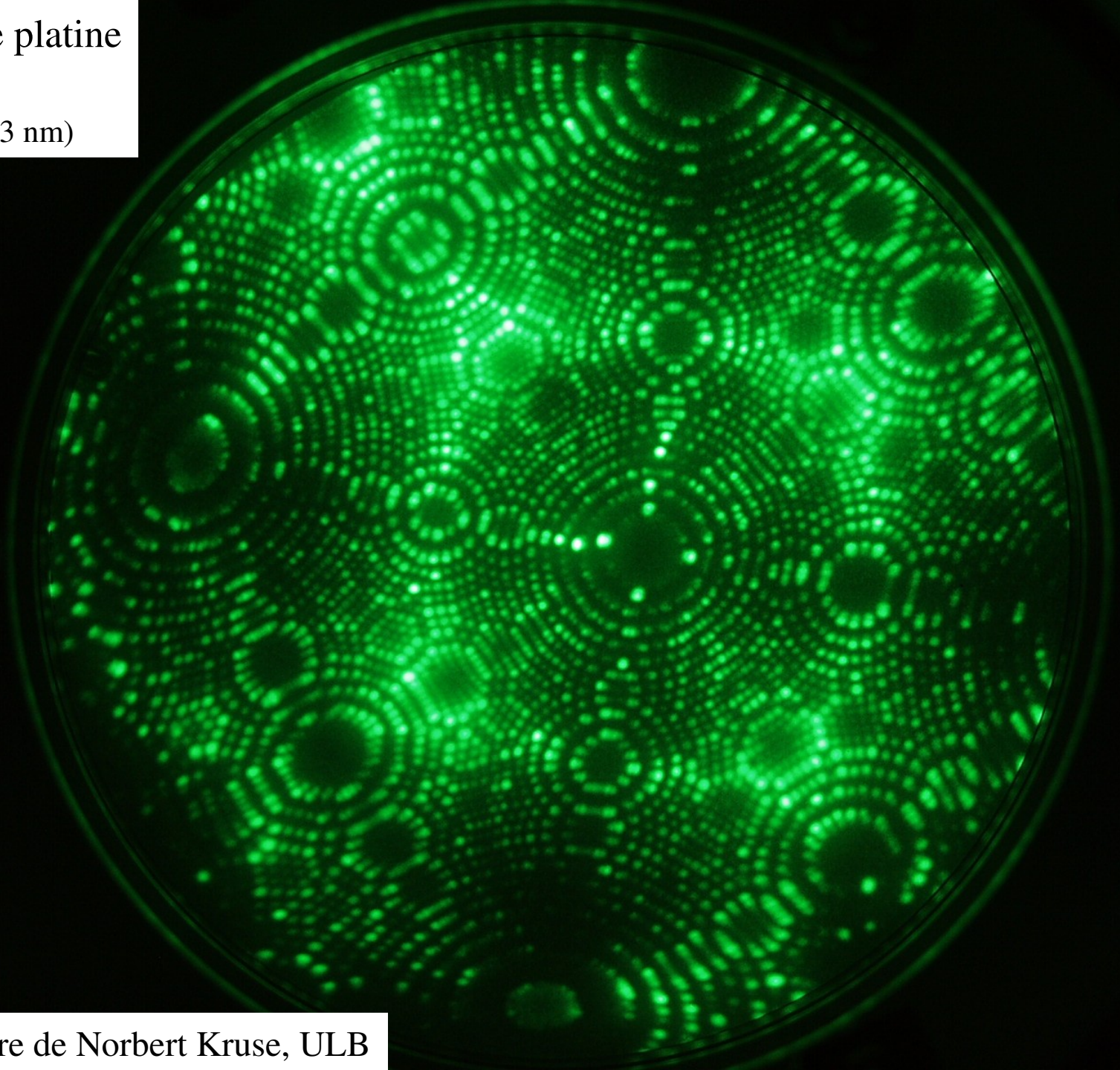
gaz révélateur: néon 55 K

champ électrique: 35 V/nm



Pointe de platine

(diamètre 63 nm)



Laboratoire de Norbert Kruse, ULB

METHODES DE MICROSCOPIE

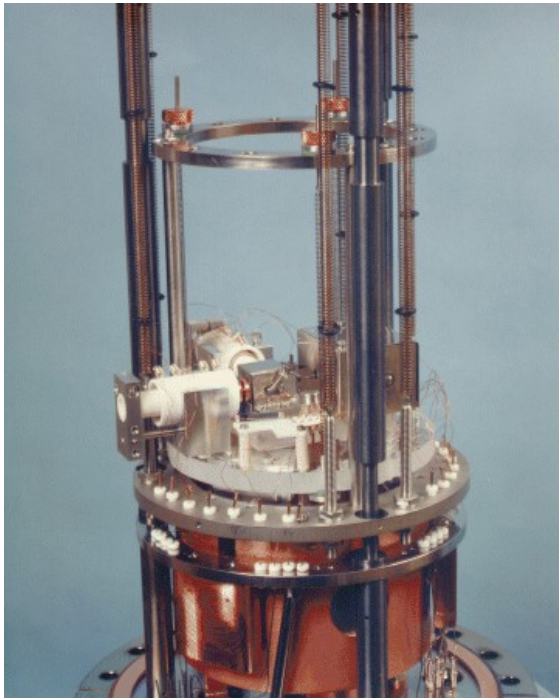
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Microscope à effet tunnel électronique

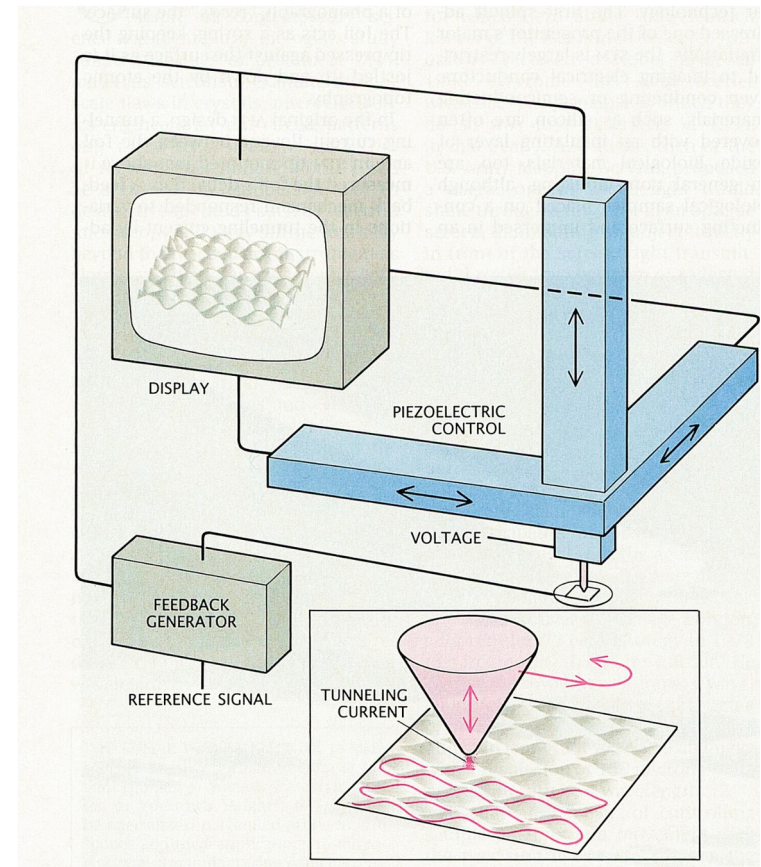
H. Rohrer & G. Binnig, laboratoire IBM, Zurich (1981)

Contrôle de la pointe
avec des piézoélectriques:

- balayage de la surface
- distance entre la pointe et la surface



NIST, USA



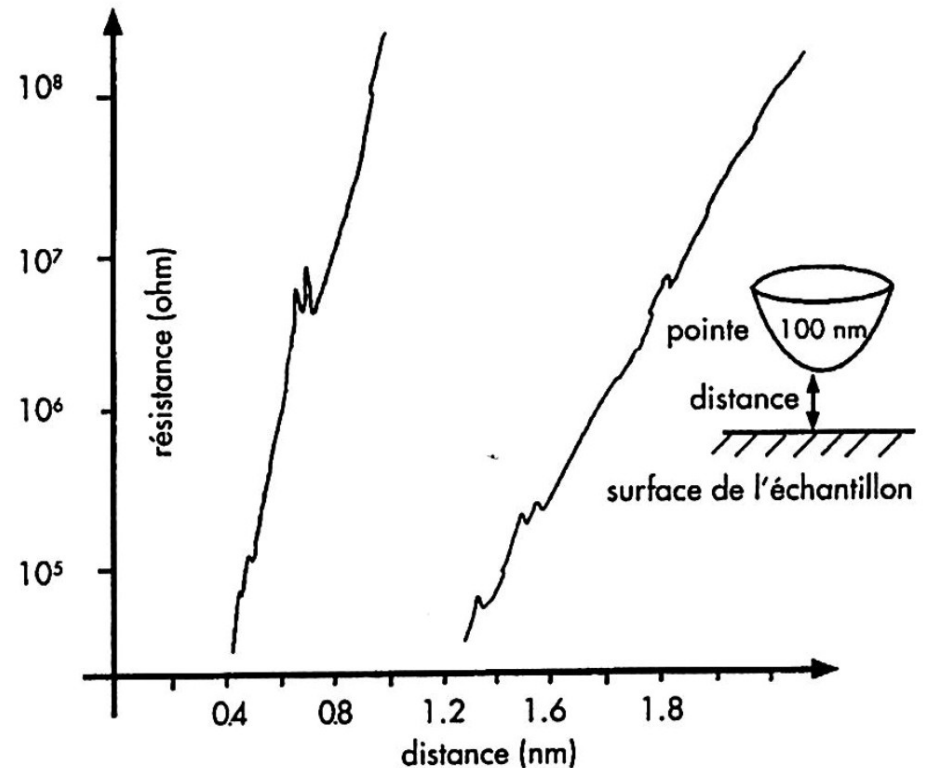
H. K. Wickramasinghe, Sci. Amer. (octobre 1989) p. 98.

Microscope à effet tunnel électronique

Effet tunnel: effet quantique

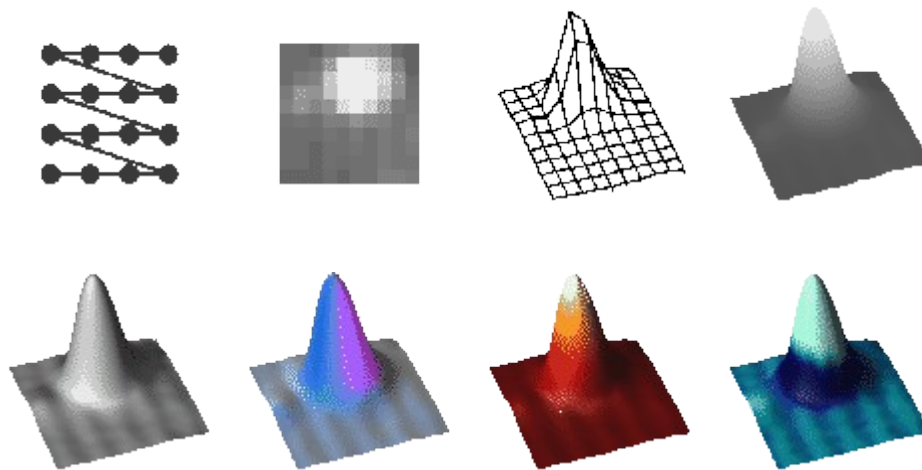
courant électrique dans le vide
entre la pointe et la surface

augmentation exponentielle
de la résistance électrique avec
la distance



Microscope à effet tunnel électronique

Le processus d'interprétation n'est pas simple ...

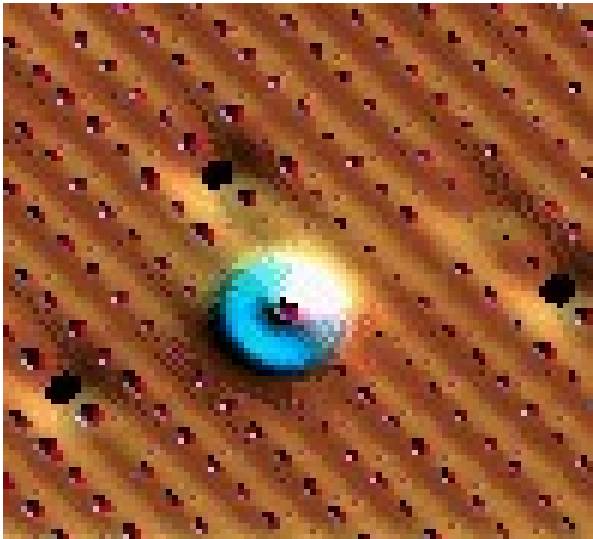


IBM Almaden, USA

Microscope à effet tunnel électronique

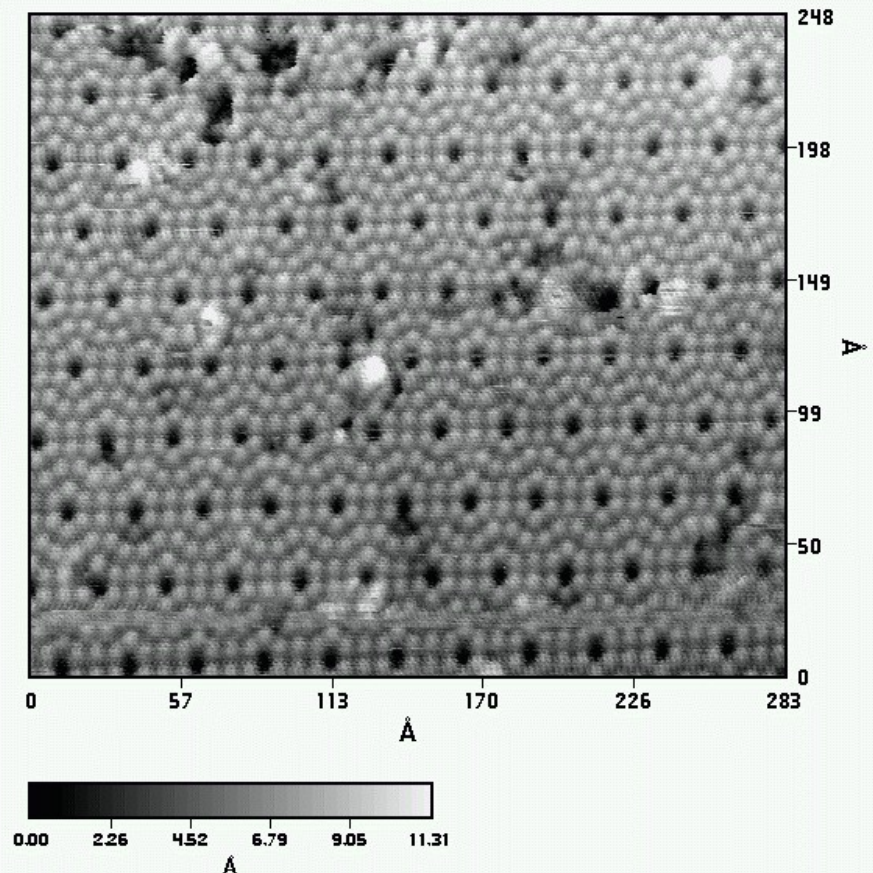
Surface de silicium

Adatomes de xénon sur
une surface de Ni



IBM Almaden, USA

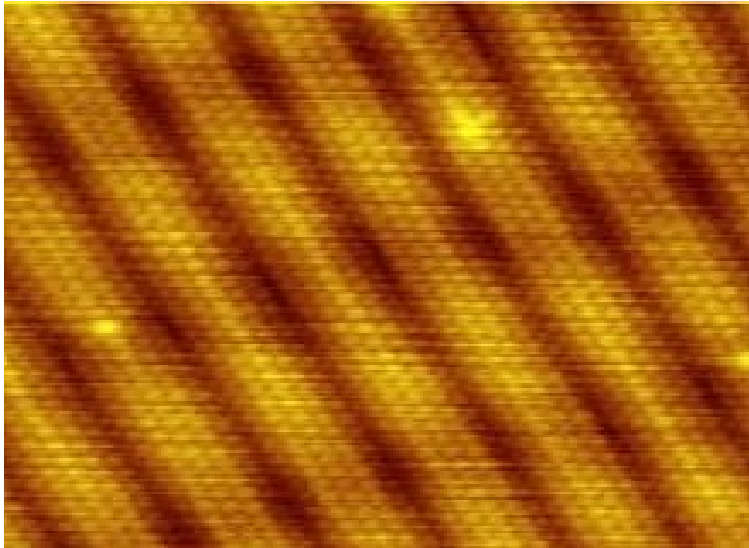
STM: Si/Si(111)



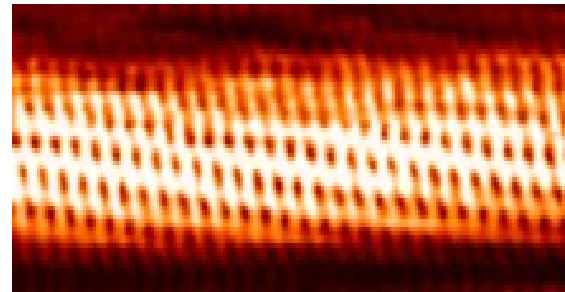
URL

Microscope à effet tunnel électronique

Image of reconstruction on a clean Gold(100) surface Erwin Rossen, Technical University Eindhoven, 2006.



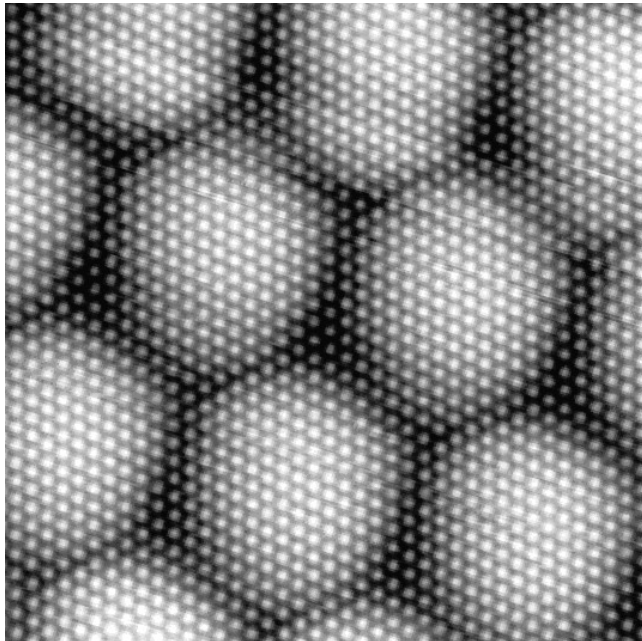
An STM image of a single-walled carbon nanotube (Taner Yildirim, The National Institute of Standards and Technology - NIST)



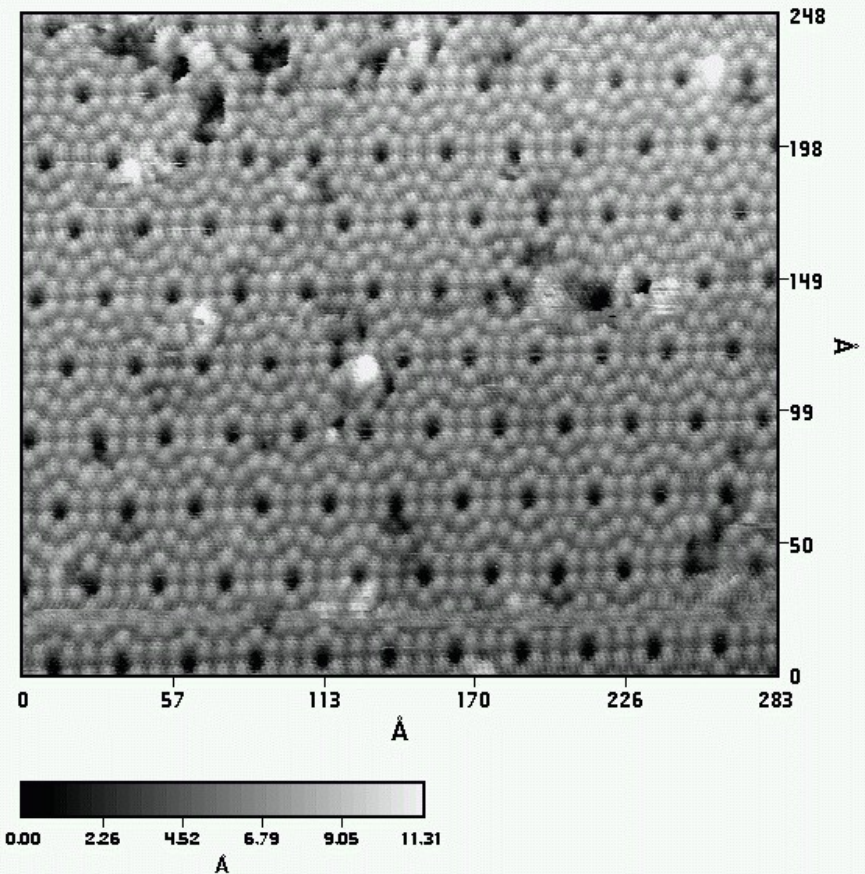
Microscope à effet tunnel électronique

Surface de silicium

Adatoms de xénon sur
une surface de graphite

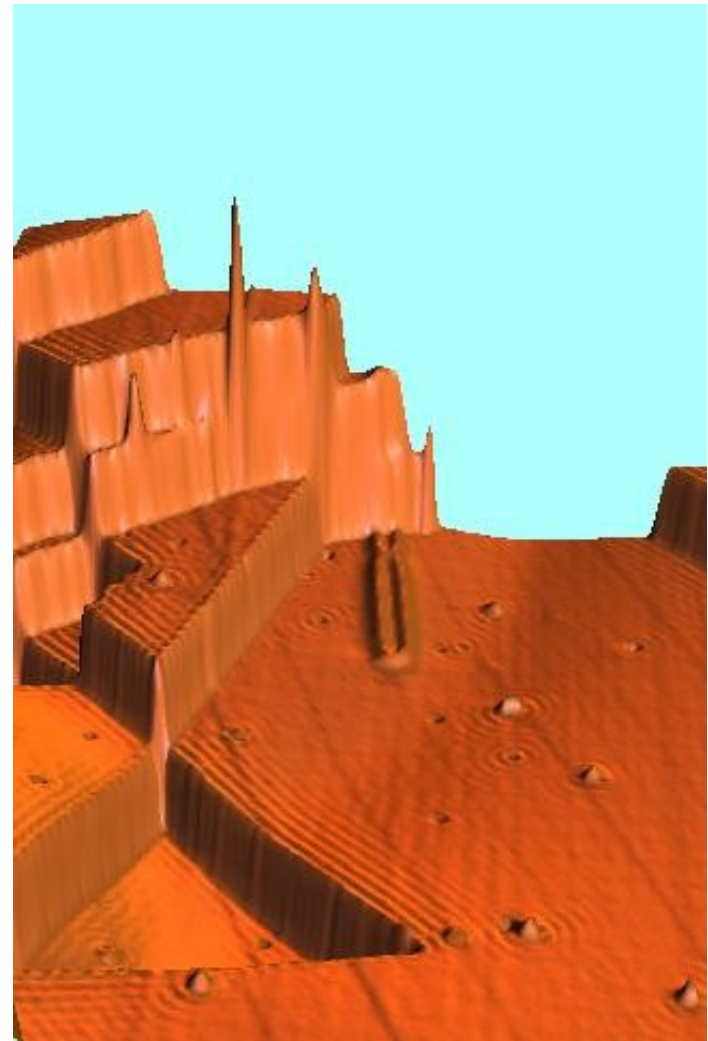


STM: Si/Si(111)

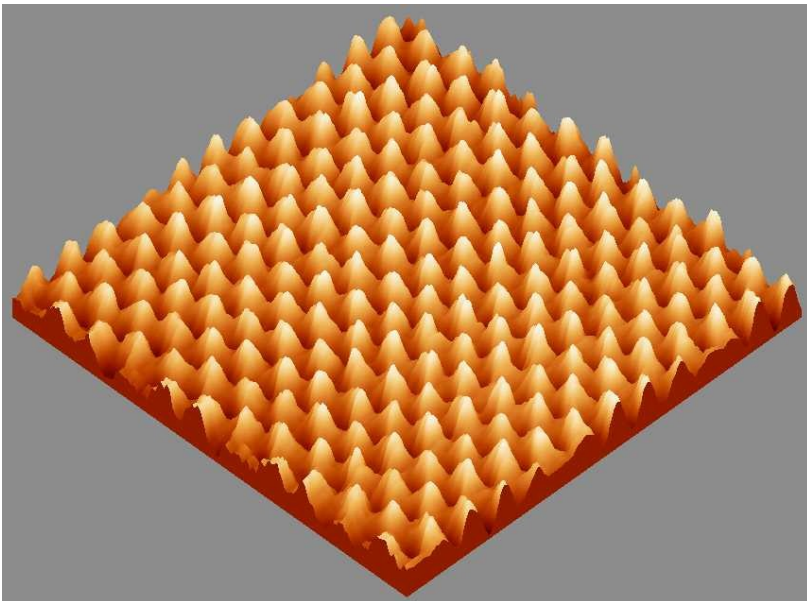


Microscope à effet tunnel électronique

Surface de cuivre



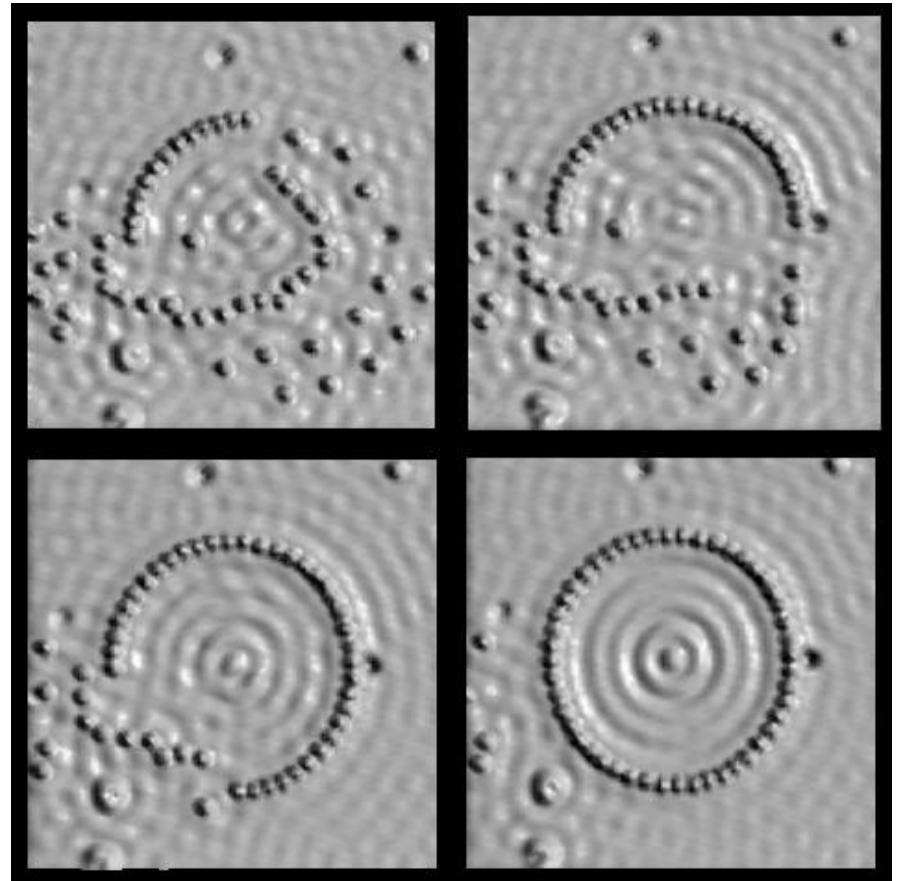
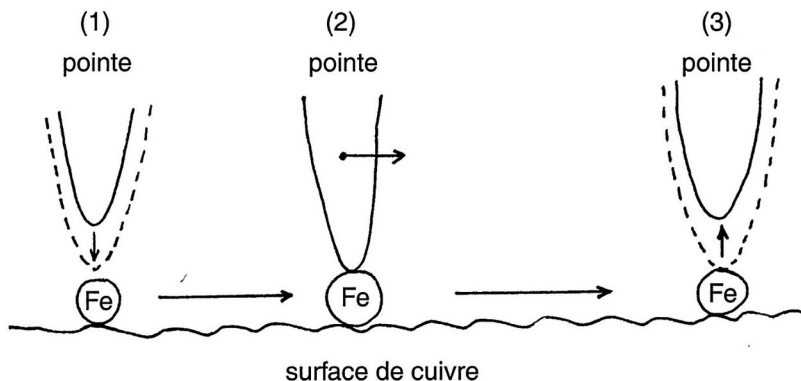
Surface de graphite



Manipulation d'atomes sur une surface

Déplacement des atomes avec la
pointe d'un microscope à effet
tunnel électronique (STM)

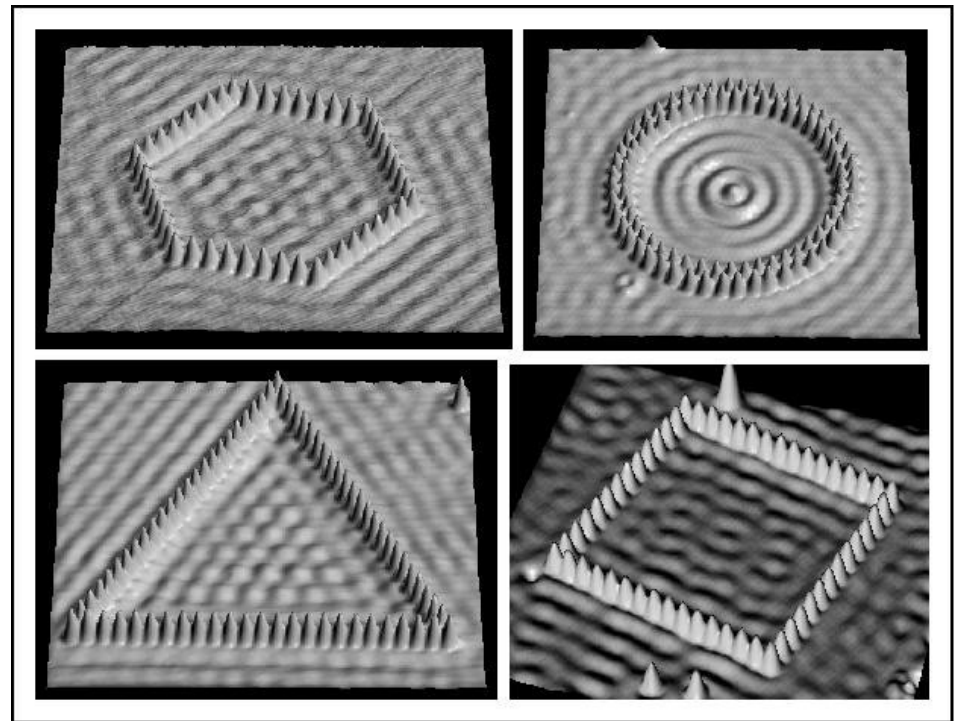
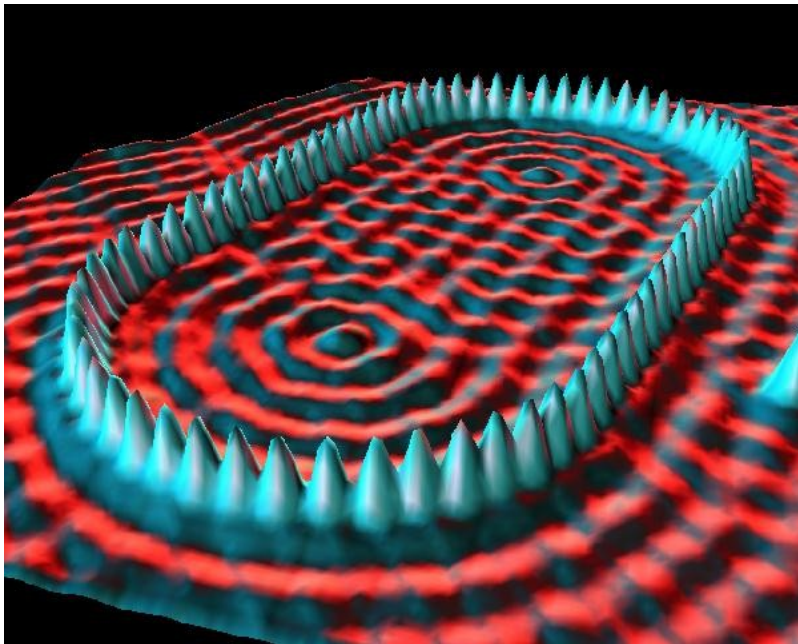
adatoms de fer
sur une surface de cuivre



Manipulation d'atomes sur une surface

Arènes quantiques:
ondes électroniques de surface

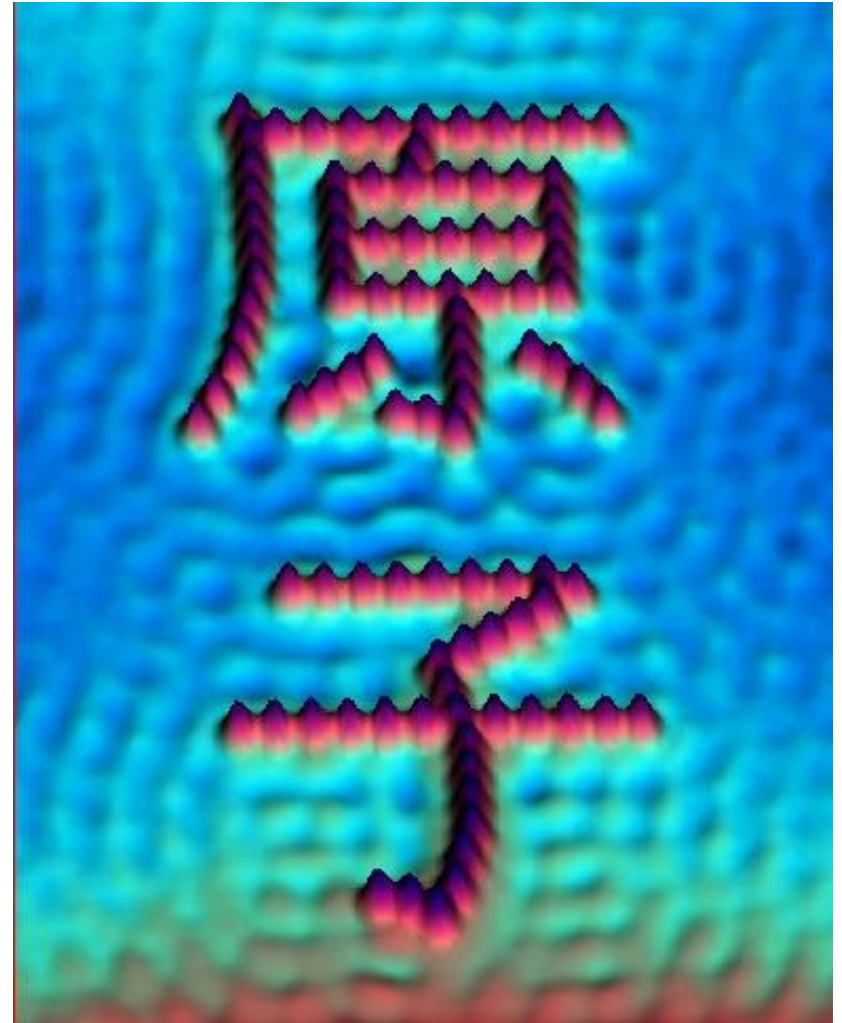
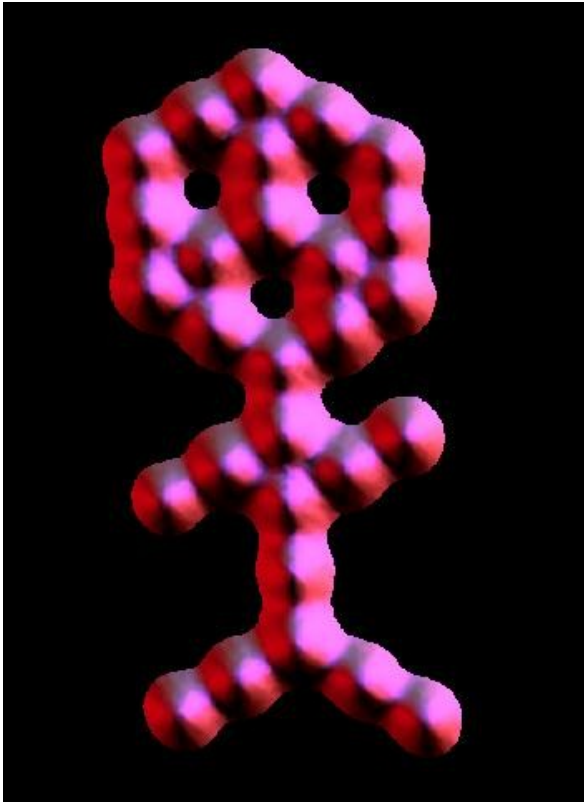
IBM Almaden, USA



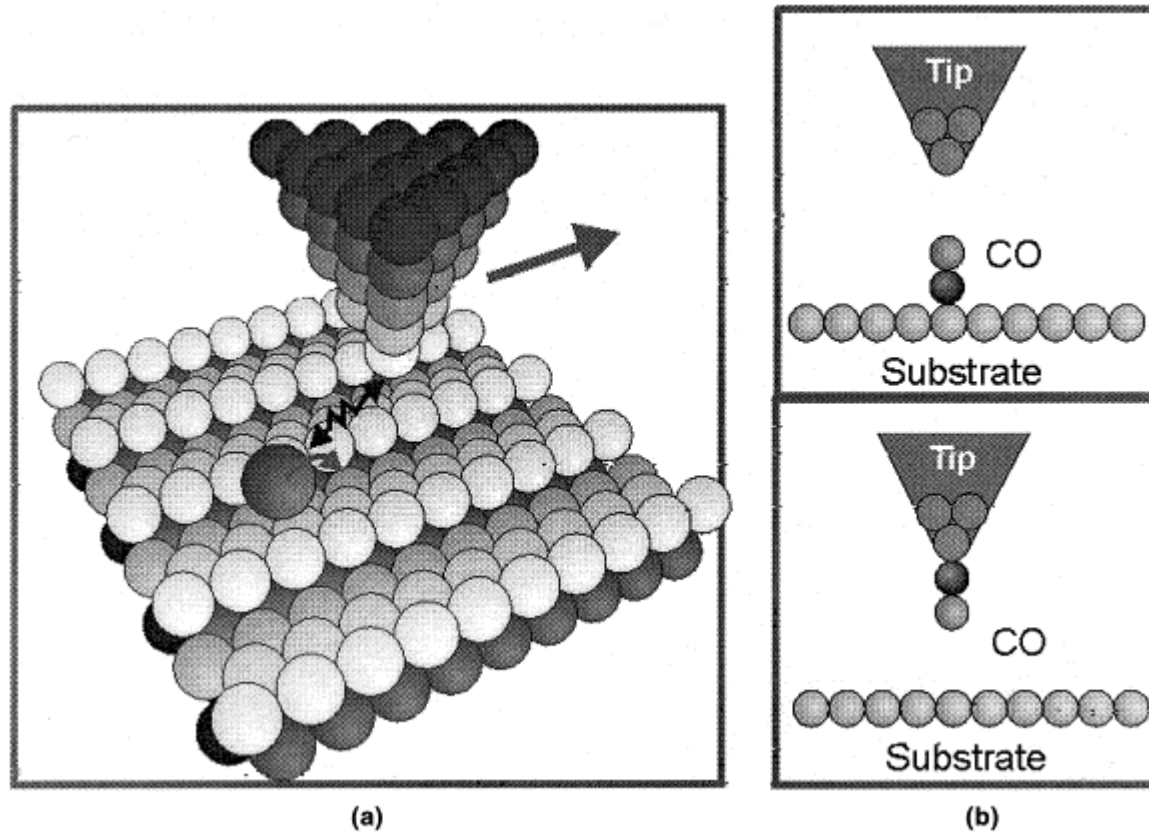
adatomes de fer
sur une surface de cuivre

Manipulation d'atomes sur une surface

Ecriture nanométrique



Manipulation



Théorie

Théorie d'effet tunnel: J. Bardeen.

“Tunneling from a many-particle point of view.”

Physical Review Letters 6 (2), 57 - 59 (1961)

Théorie de STM: J. Tersoff and D. R. Hamann.

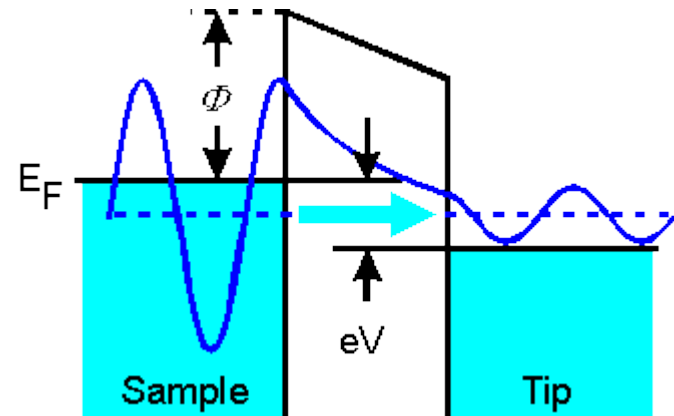
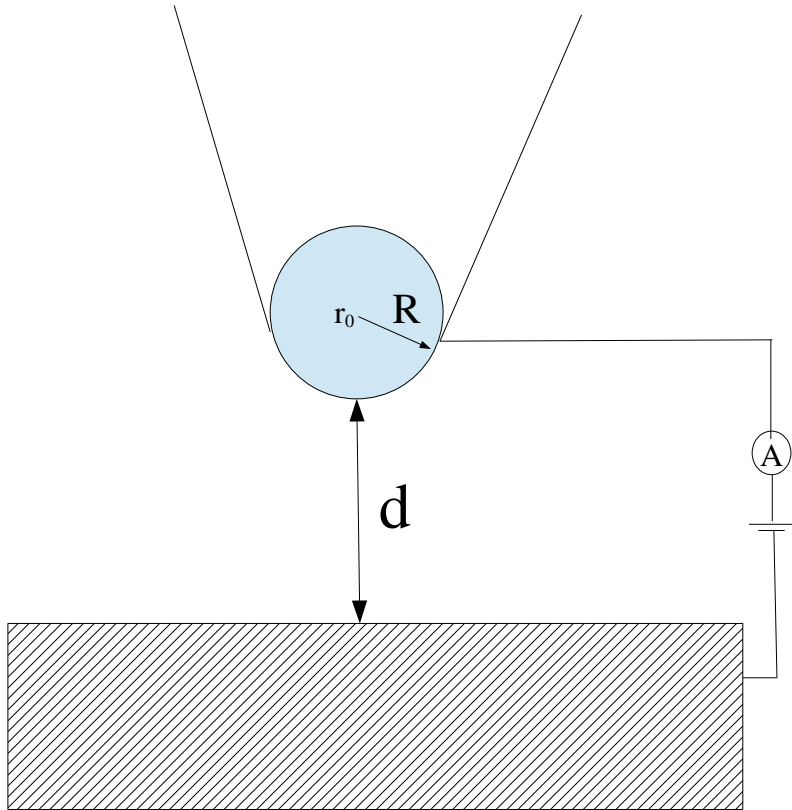
“Theory and application for the scanning tunneling microscope.”

Physical Review Letters 50 (25), 1998 - 2001 (1983)

Voir aussi: <http://www.alexgottlieb.com/Papers/Duke.pdf>

Courant de tunnel

Biais V



<http://www.fkp.uni-erlangen.de/methoden/stmtutor/stmtheo.html>

$d \sim 1\text{nm}$

courant $\sim 10\text{pA}-10\text{nA}$

balayage d'elements piezoelectric avec précision $\sim 10^{-3}\text{nm}$

Théorie de Bardeen (tunneling rate)

Hypothèses

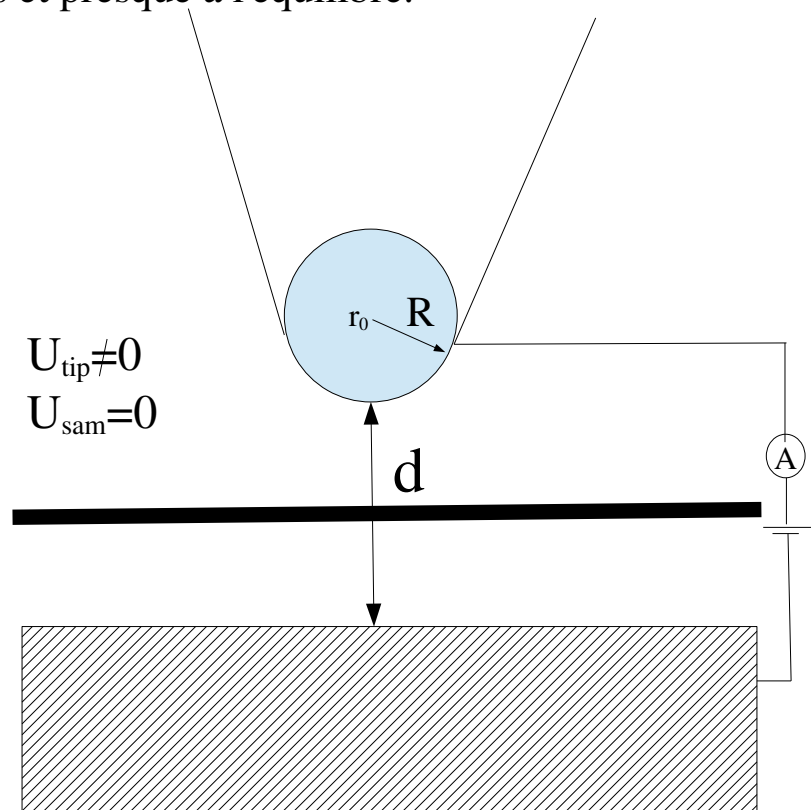
1. Les états de la pointe et l'échantillon sont presque orthogonales.
2. L'effet tunnel est faible: donc, la théorie de perturbation du premier ordre est suffisante.
3. Les électrons sont indépendants (de façon équivalente: on parle des quasi-particules).
4. Les conditions sont stationnaires et presque à l'équilibre.

$$H = T + U_s + U_{\text{tip}} \quad T = \sum_{n=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2$$

$$H_{\text{sam}} = T + U_{\text{sam}} \quad H_{\text{sam}} \psi_{\text{sam}} = W_{\text{sam}} \psi_{\text{sam}}$$

$$H_{\text{tip}} = T + U_{\text{tip}} \quad H_{\text{tip}} \varphi_{\text{tip}}^{(n)} = W_{\text{tip}}^{(n)} \varphi_{\text{tip}}^{(n)}$$

$$U_{\text{tip}} = 0 \\ U_{\text{sam}} \neq 0$$



Ansatz

$$\Psi(t) = e^{iW_{\text{sam}}t/\hbar} \psi_{\text{sam}} + \sum_n a_n(t) \phi_{\text{tip}}^n$$

Schrodinger equation: $i\hbar \frac{d}{dt} \Psi(t) = H \Psi(t)$

$$\Rightarrow i\hbar \sum_n \frac{da_n(t)}{dt} \phi_{\text{tip}}^n = e^{iW_{\text{sam}}t/\hbar} (H - W_{\text{sam}}) \psi_{\text{sam}} + \sum_n a_n(t) \underbrace{(H - H_{\text{tip}} + W_{\text{tip}}^n)}_{=0} \phi_{\text{tip}}^n$$

Multiply by $\phi_{\text{tip}}^{(m)}$ and integrate:

$$\begin{aligned} i\hbar \frac{da_m(t)}{dt} &= e^{iW_{\text{sam}}t/\hbar} \left\langle \phi_{\text{tip}}^{(m)} \left| (H - H_{\text{sam}}) \right| \psi_{\text{sam}} \right\rangle + \sum_n a_n(t) \left\langle \phi_{\text{tip}}^{(m)} \left| (W_{\text{tip}}^n + H - H_{\text{tip}}) \right| \phi_{\text{tip}}^{(n)} \right\rangle \\ &= e^{iW_{\text{sam}}t/\hbar} \left\langle \phi_{\text{tip}}^{(m)} \left| (H - H_{\text{sam}}) \right| \psi_{\text{sam}} \right\rangle + W_{\text{tip}}^{(m)} a_m(t) + \sum_n a_n(t) \left\langle \phi_{\text{tip}}^{(m)} \left| \underbrace{(H - H_{\text{tip}})}_{U_{\text{sam}}} \right| \phi_{\text{tip}}^{(n)} \right\rangle \end{aligned}$$

Now, if (e.g. at short times) $a_{(n)}(t) \ll 1$ then the last term can be neglected and the rest integrated to get

$$\begin{aligned} a_m(t) &= \frac{1}{i\hbar} \left\langle \phi_{\text{tip}}^{(m)} \left| H - H_{\text{sam}} \right| \psi_{\text{sam}} \right\rangle \int_0^t e^{-i(W_{\text{sam}} - W_{\text{tip}}^{(m)})s/\hbar} ds \\ &= \frac{1}{i\hbar} \left\langle \phi_{\text{tip}}^{(m)} \left| H - H_{\text{sam}} \right| \psi_{\text{sam}} \right\rangle \frac{e^{-i(W_{\text{sam}} - W_{\text{tip}}^{(m)})t/\hbar} - 1}{W_{\text{sam}} - W_{\text{tip}}^{(m)}} \sin\left(\frac{(W_{\text{sam}} - W_{\text{tip}}^{(m)})t}{2\hbar}\right) \\ &= \frac{1}{i\hbar} \left\langle \phi_{\text{tip}}^{(m)} \left| H - H_{\text{sam}} \right| \psi_{\text{sam}} \right\rangle 2e^{-i(W_{\text{sam}} - W_{\text{tip}}^{(m)})t/2\hbar} \frac{\sin\left(\frac{(W_{\text{sam}} - W_{\text{tip}}^{(m)})t}{2\hbar}\right)}{W_{\text{sam}} - W_{\text{tip}}^{(m)}} \end{aligned}$$

$$\begin{aligned}
P(t) &= \sum_m \left| \langle \phi_{\text{tip}}^{(m)} | \Psi(t) \rangle \right|^2 \\
&= \sum_m \left| \langle \phi_{\text{tip}}^{(m)} | H - H_{\text{sam}} | \psi_{\text{sam}} \rangle \right|^2 4 \frac{\sin^2 \left(\frac{(W_{\text{sam}} - W_{\text{tip}}^{(m)}) t}{2 \hbar} \right)}{(W_{\text{sam}} - W_{\text{tip}}^{(m)})^2} \\
&= \int_{-\infty}^{\infty} \left| \langle \phi_{\text{tip}}(W) | H - H_{\text{sam}} | \psi_{\text{sam}} \rangle \right|^2 4 \frac{\sin^2 \left(\frac{(W_{\text{sam}} - W) t}{2 \hbar} \right)}{(W_{\text{sam}} - W)^2} \rho(W) dW
\end{aligned}$$

where the density of states is $\rho(W) = \sum_m \delta(W - W_{\text{tip}}^{(m)})$

Because $\frac{\sin^2(x)}{x^2}$ is strongly peaked near the origin, we can approximate

$$\begin{aligned}
P(t) &\approx \left| \langle \phi_{\text{tip}}(W_{\text{sam}}) | H - H_{\text{sam}} | \psi_{\text{sam}} \rangle \right|^2 4 \rho(W_{\text{sam}}) \int_{-\infty}^{\infty} \frac{\sin^2 \left(\frac{(W_{\text{sam}} - W) t}{2 \hbar} \right)}{(W_{\text{sam}} - W)^2} dW \\
&= \frac{2\pi t}{\hbar} \left| \langle \phi_{\text{tip}}(W_{\text{sam}}) | H - H_{\text{sam}} | \psi_{\text{sam}} \rangle \right|^2 \rho(W_{\text{sam}})
\end{aligned}$$

Théorie de Tersoff et Hamann (theory of TEM)

Hypothèses

1. Les états de la pointe et l'échantillon sont presque orthogonales.
2. L'effet tunnel est faible: donc, la théorie de perturbation du premier ordre est suffisante.
3. Les électrons sont indépendants (de façon équivalente: on parle des quasi-particules).
4. Les conditions sont stationnaires et presque à l'équilibre.

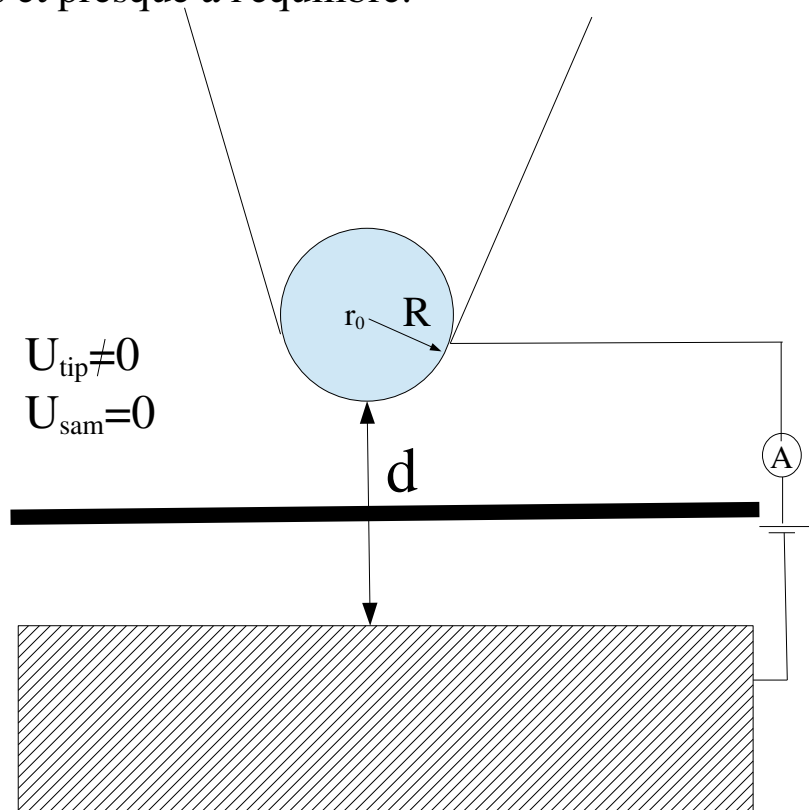
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$$H_{\text{tip}} = T + U_{\text{tip}} \quad H_{\text{tip}} \varphi_{\text{tip}}^{(n)} = W_{\text{tip}}^{(n)} \varphi_{\text{tip}}^{(n)}$$

$$U_{\text{tip}} = 0$$

$$U_{\text{sam}} \neq 0$$



$$U_{\text{tip}} \neq 0$$

$$U_{\text{sam}} = 0$$

I. la courant

Rappelez-vous que

$$P(t; W_{sam}) = \frac{2\pi t}{\hbar} \left| \langle \phi_{tip}(W_{sam}) | (H - H_{sam}) | \psi_{sam} \rangle \right|^2 \rho_{tip}(W_{sam})$$

Ca, c'est le probabilité quand tous les états de la point ne sont pas occupés et tous les états de l'échantillon sont occupés. En effet, la fraction des états occupés suivre la distribution Fermi-Dirac. Alors, la courant est

$$I = e \sum_{sam} f(W_{sam}; \mu_{sam}) (1 - f(W_{sam}; \mu_{tip})) \frac{dP(t; W_{sam})}{dt}$$

$$\Rightarrow e \sum_{sam} \Theta(\mu_{sam} - W_{sam}) \Theta(W_{sam} - \mu_{tip}) \frac{dP(t; W_{sam})}{dt}$$

II. éléments de la matrice

Dehors la pointe $-\frac{\hbar^2}{2m} \nabla^2 \phi_{tip}^n = W_{tip}^n \phi_{tip}^n$

Chen, Phys. Rev. B 42, 8841 (1990)
 "Tunneling matrix elements in 3 dim. space"

En general $\phi_{tip}^n(\mathbf{r}) = \sum_{lm} C_{lm} f_l(\kappa |\mathbf{r} - \mathbf{r}_0|) Y_{lm}(\theta, \phi), \quad \kappa = (2mW_{tip}^n)^{1/2} / \hbar$

$$\frac{d}{du} u^2 \frac{df_l(u)}{du} - (u^2 + l(l+1)) f(u) = 0 \Rightarrow \text{spherical modified Bessel functions}$$

s-wave tip $\phi_{tip}^n(\mathbf{r}) \approx C_{00} f_0(\kappa |\mathbf{r} - \mathbf{r}_0|) Y_{00}(\theta, \phi) = A \exp(-\kappa |\mathbf{r} - \mathbf{r}_0|) / (\kappa |\mathbf{r} - \mathbf{r}_0|)$

II. éléments de la matrice

Nous avons besoin de $\langle \phi_{tip}(W_{sam}) | (H - H_{sam}) | \psi_{sam} \rangle$

$$\phi_{tip}(W_{sam}) \equiv \phi_{tip}^m$$

En supposant que $W_{sam} \sim W_{tip}$, Bardeen a montré (exercice!) que

$$\langle \phi_{tip}(W_{sam}) | (H - H_{sam}) | \psi_{sam} \rangle \simeq \frac{-\hbar^2}{2m} \int_{\partial tip} \{ \phi_{tip}^{m*} \nabla \psi_{sam} - \psi_{sam} \nabla \phi_{tip}^{m*} \} d\mathbf{r}$$

$$\text{(Green's theorem)} \quad \simeq \frac{-\hbar^2}{2m} \int_{tip} \{ \phi_{tip}^{m*} \nabla^2 \psi_{sam}^* - \psi_{sam} \nabla^2 \phi_{tip}^{*m} \} d\mathbf{r}$$

$$\simeq \int_{tip} \{ \phi_{tip}^{m*} W_{sam} \psi_{sam} - \frac{-\hbar^2}{2m} \psi_{sam} \nabla^2 \phi_{tip}^{*m} \} d\mathbf{r}$$

$$\simeq - \int_{tip} \psi_{sam} \left\{ \frac{-\hbar^2}{2m} \nabla^2 - W_{tip} \right\} \phi_{tip}^{*m} d\mathbf{r}$$

$$\simeq - \frac{\hbar^2}{2m} 4\pi A \psi_{sam}(\mathbf{r}_0)$$

III. conclusions

$$I = e \sum_{sam} f(W_{sam}; \mu_{sam}) (1 - f(W_{sam}; \mu_{tip})) \frac{dP(t; W_{sam})}{dt}$$

$$\simeq e \sum_{sam} \Theta(\mu_{sam} - W_{sam}) \Theta(W_{sam} - \mu_{tip}) \rho_{tip}(W_{sam}) \times$$

$$\frac{2\pi}{\hbar} |\langle \phi_{tip}(W_{sam}) | (H - H_{sam}) | \psi_{sam} \rangle|^2$$

$$I \simeq e \sum_{sam} \Theta(\mu_{sam} - W_{sam}) \Theta(W_{sam} - \mu_{tip}) \rho_{tip}(W_{sam}) \frac{2\pi}{\hbar} \left(4\pi \frac{\hbar^2}{2m} A \psi_{sam}(\mathbf{r}_0) \right)^2$$

Donc, pour un biais faible

$$\lim_{eV \ll E_f} I = \frac{2\pi}{\hbar} \left(\frac{\hbar^2}{2m} 4\pi \right)^2 A^2 e \rho_{tip}(W_{sam}) \sum_{\mu_{sam} > W_{sam} > \mu_{tip}} |\psi_{sam}(\mathbf{r}_0)|^2, \quad \mu_{tip} \leq \mu \leq \mu_{sam}$$

$$= \frac{\hbar^3}{m^2} A^2 e (\mu_{sam} - \mu_{tip}) \rho_{tip}(W_{sam}) \rho_{sam}(W_{sam}; \mathbf{r}_0)$$

$$= \frac{\hbar^3}{m^2} A^2 e V \rho_{tip}(\mu) \rho_{tip}(W_{sam}) \rho_{sam}(W_{sam}; \mathbf{r}_0)$$

Parce-que $\psi_{sam}(\mathbf{r}_0) \sim e^{-\kappa(R+d)}$ il s'ensuite que $\lim_{eV \ll E_f} I \sim e^2 V e^{-2\kappa(R+d)}$

et la resolution lateral est determinee par $e^{-2\kappa R} = e^{-2\kappa\sqrt{d^2 + x^2}} \sim e^{-2\kappa d(1 + \frac{x^2}{2d^2})} = e^{-2\kappa d} e^{-\left(\frac{x}{d/2\kappa}\right)^2}$

donc $\Delta x \sim d/2\kappa$

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Cryo-TEM

2017 Prix Nobel: Frank, Dubochet and Henderson

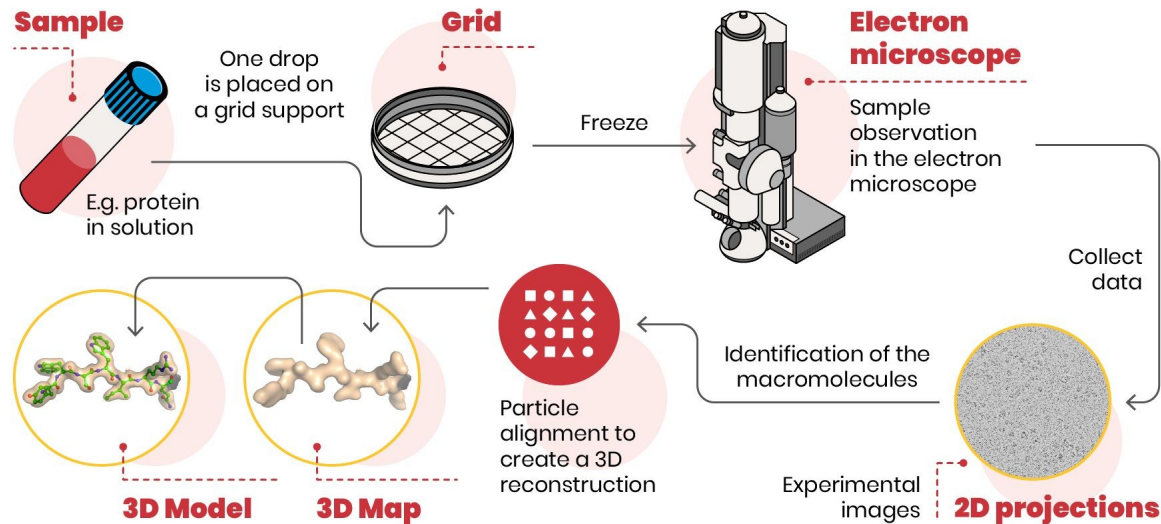
Problems with TEM for Biological molecules:

- sensitive to damage by TEM beam
- drying in vacuum (water is important in biology!)

Solution: freeze to preserve water & protect sample

Problem: crystalline ice scatters TEM beam

Solution: flash freeze to produce amorphous ice



Cryo-TEM

DUBOCHET'S VITRIFICATION METHOD

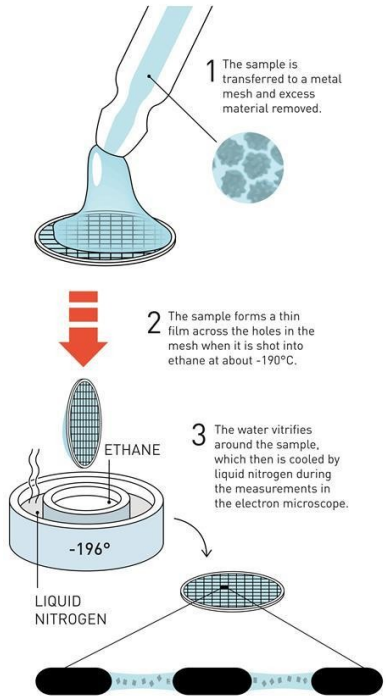
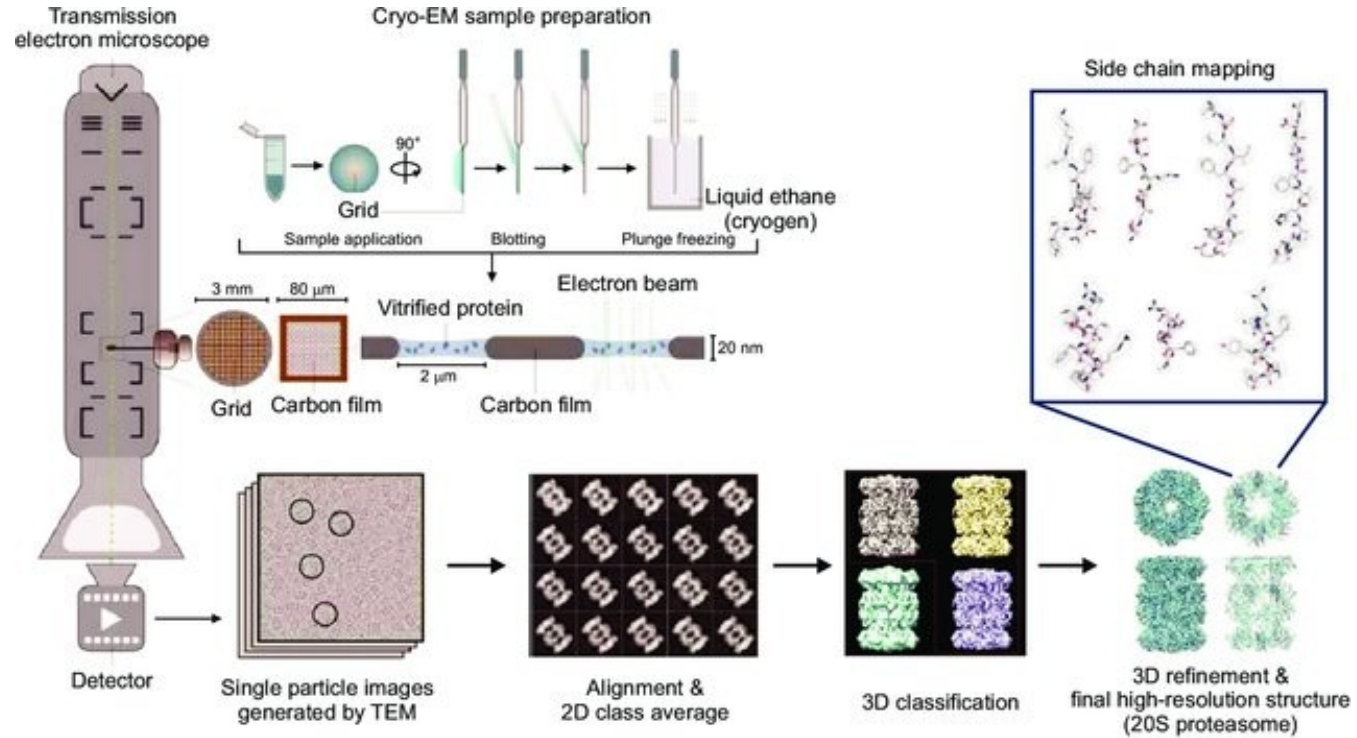
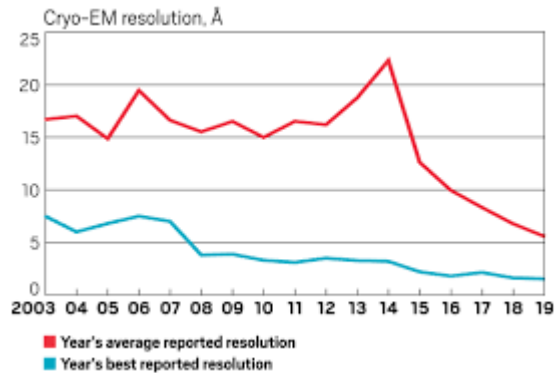


Illustration: ©Johan Jarnestad/The Royal Swedish Academy of Sciences

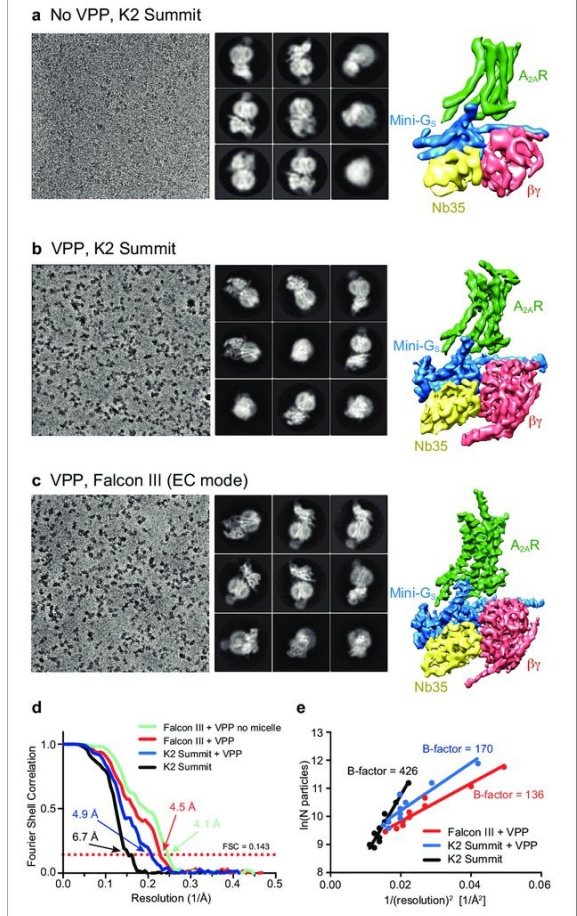


Determination of high-resolution structure through image processing

Cryo-TEM



The potential: atomic-scale resolution of macromolecules without need for crystallization

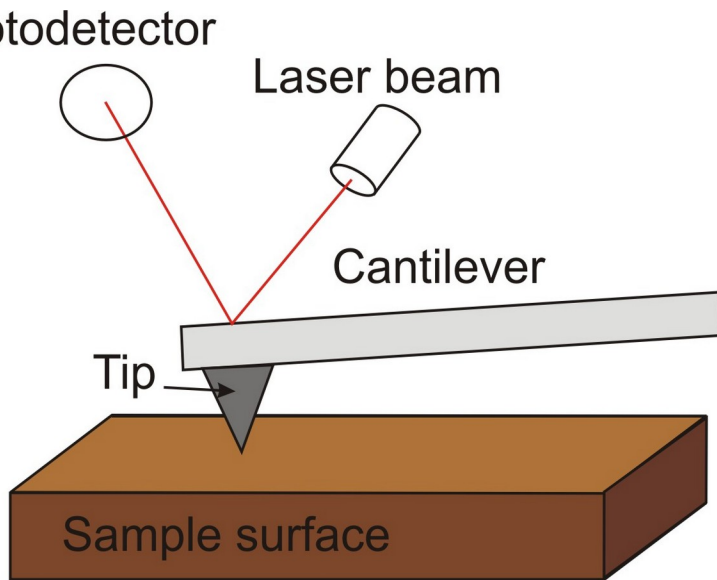


Drawbacks: time-consuming, expensive, sample preparation is difficult

METHODES DE MICROSCOPIE

- Paramètres Fondamentaux
- Microscopes Optiques
 - Principe
 - Améliorations: phase contrast, dark field, fluorescent, ...
 - Cristallographe aux Rayon X
- Microscope Electronique
 - à Transmission
 - à Balayage
- Microscope à emission champ
- Microscope à effet tunnel électronique
- Cryo-TEM
- **Microscope à force atomique**
- Optical Tweezers
- Light Scattering

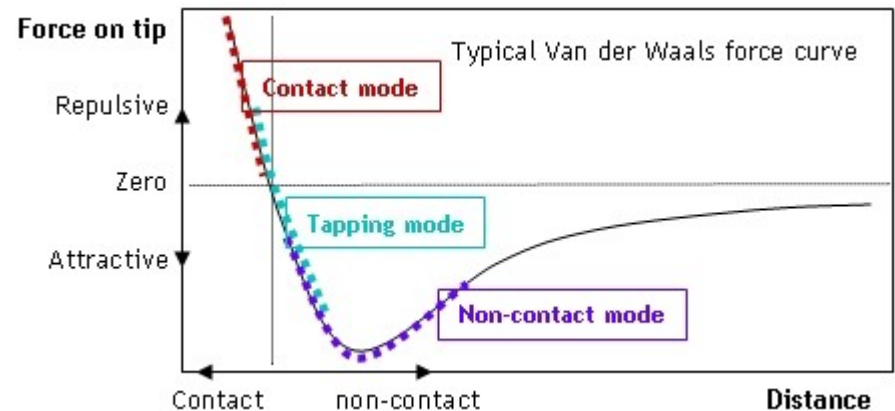
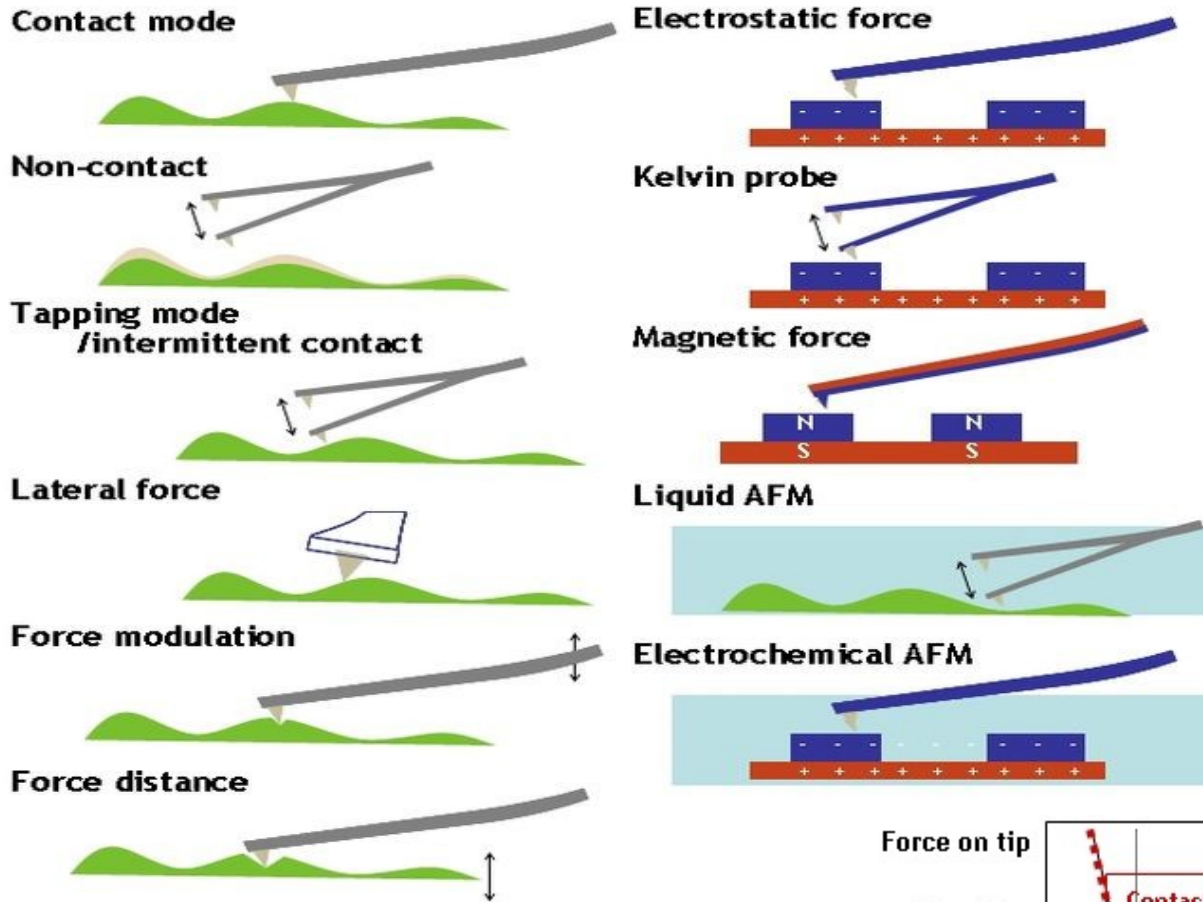
Microscope à force atomique



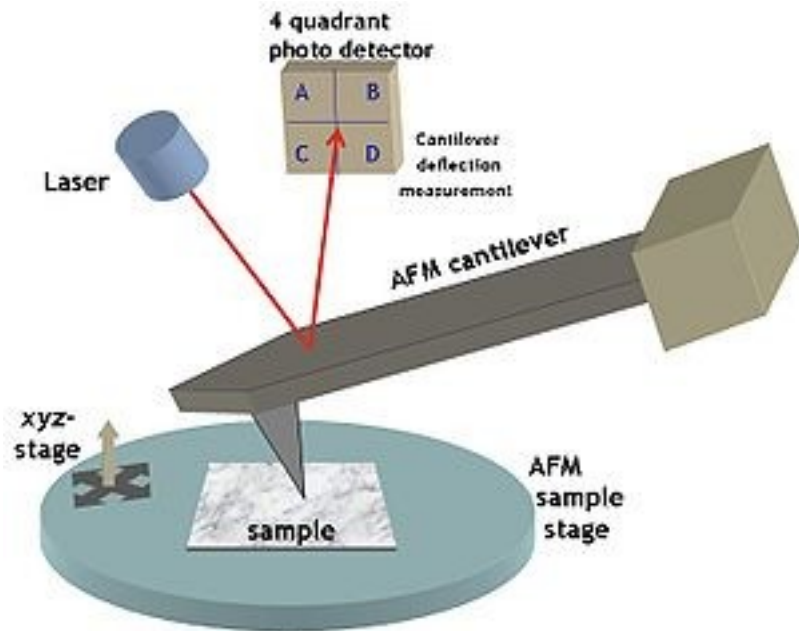
	STM	AFM
Lateral Resolution	0.5-1 nm	0.5 nm
Vertical Resolution	2D only	0.05nm
Field of view	1-2 X 1-2 mm	100 x 100 μm
Vertical range		100 μm
Preparation	Couche conductrice	----
Environment	vide	L'air, liquide

Kurganskaya, I.; Lutge, A.; Barron, A. The Application of VSI (Vertical Scanning Interferometry) to the Study of Crystal Surface Processes, Connexions Web site. <http://cnx.org/content/m22326/1.4/>, Jul 13, 2009.

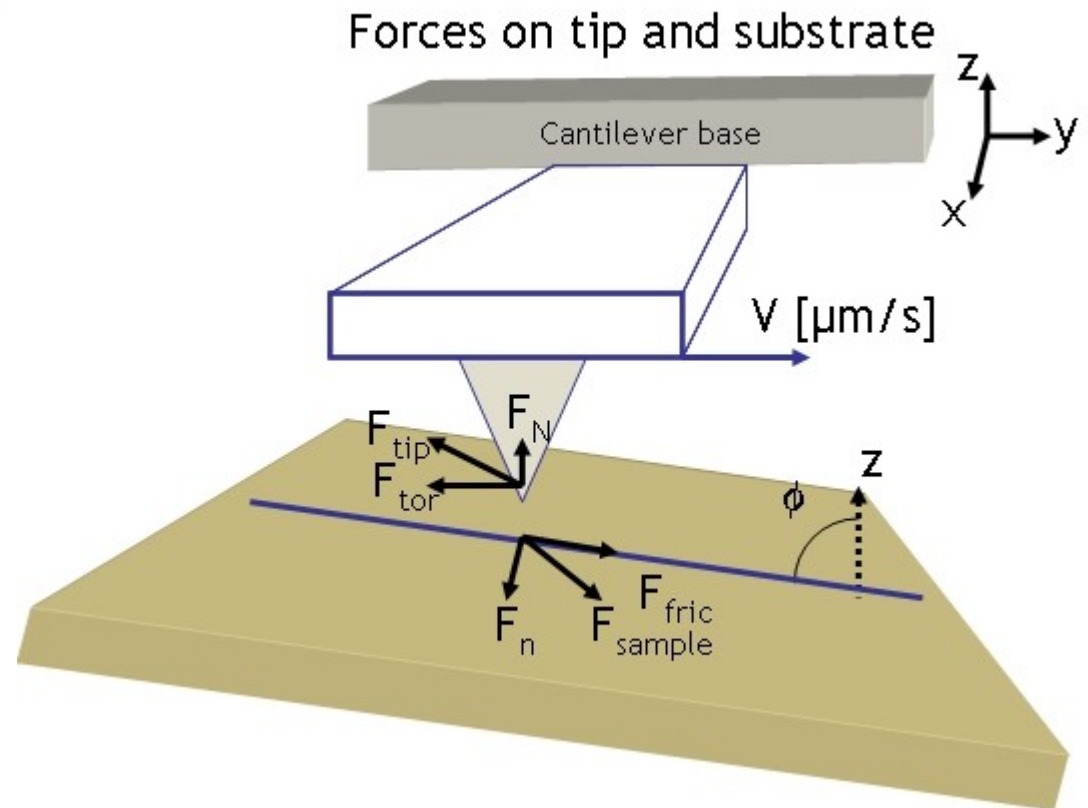
AFM: les modes de fonctionnement



Microscope à force atomique



Signal de droit-gauche: $A+C-(B+D)$
Signal de haut en bas: $A+B-(C+D)$



Microscope à force atomique

I. PRINCIPE GÉNÉRAL: UNE OSCILLATEUR CLASSIQUE

$$\ddot{u} + 2\gamma\dot{u} + \omega_0^2 u = \cos t + \frac{1}{m} F(D, u)$$

ou

D = distance entre la surface et la position de la pointe quand le cantilever n'est pas déflecté.

z = distance entre la surface et la position de la pointe actuelle

$u = z - D$ = déviation

m = masse effective

$\omega_0 = \sqrt{\frac{k}{m}}$ = la fréquence de résonance de l'oscillateur

k = la raideur du cantilever

γ = un terme de dissipation

A = l'amplitude de l'excitation

ω = fréquence de l'excitation

$F(D, u)$ = la force d'interaction pointe-surface

N.B. $Q = \frac{\omega_0}{2\gamma}$ est le facteur de qualité.

Microscope à force atomique

II. CASE I: CONTACT MODE

Ne pas d'excitation:

$$\ddot{u} + 2\dot{u} + \frac{1}{m}u = \frac{1}{m}F(D, u) \Rightarrow ku = F(D, u)$$

e.g.

$$ku \simeq F(D) + uF'(D) \Rightarrow u = \frac{F(D)}{k + F'(D)}, \text{ Si } k \gg F'(D), u \simeq \frac{F(D)}{k}$$

III. CASE II: LE MODE RÉSONNANT LINÉAIRE

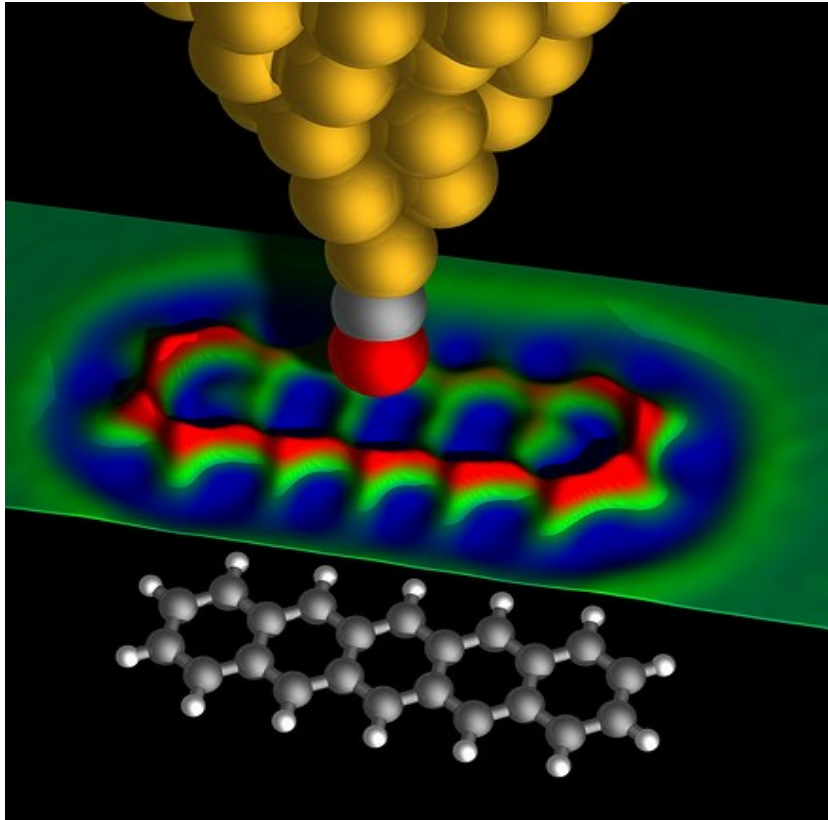
$$\ddot{u} + 2\dot{u} + \frac{1}{m}u \simeq \cos t + \frac{1}{m}F(D) + u\frac{1}{m}F'(D)$$

desorte que

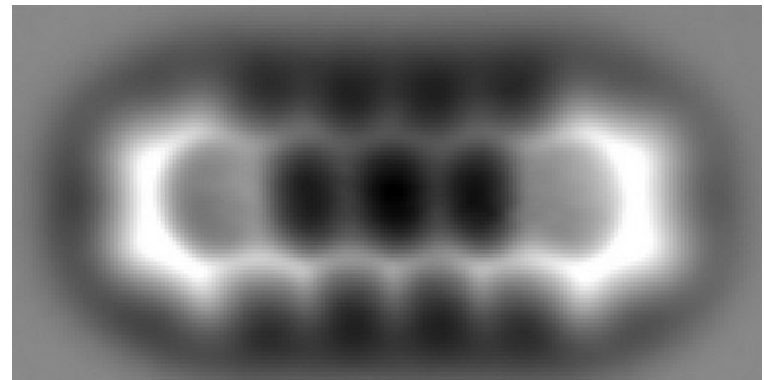
$$\ddot{u} + 2\dot{u} + \frac{1}{m}u \simeq \frac{1}{k}F'(D) u \simeq \cos t + \frac{1}{m}F(D)$$

Ça veut dire qu'il y a un changement de fréquence naturelle de l'oscillateur

AFM Recherche actuelle ...



Imaging the "anatomy" of a pentacene molecule - 3D rendered view: By using an atomically sharp metal tip terminated with a carbon monoxide (CO) molecule, IBM scientists were able to measure in the short-range regime of forces which allowed them to obtain an image of the inner structure of the molecule. The colored surface represents experimental data. (Image courtesy of IBM Research/Zurich)



Resume

	Optique	Xray	Confocal	TEM/SEM	STM	AFM
Lateral Resolution	200nm	25nm	200nm	0.1nm/3nm	0.1 nm	0.5 nm
Vertical Resolution	2D only	-----	500nm	-----	2D only	0.05nm
Field of view	grande	50 μ m	grande	Bayalage	1-2 X 1-2 mm	100 x 100 μ m
Vertical range	-----	-----	Limité par le temps (1-1000 sec/mm ² /tranche)	-----	-----	100 μ m
Preparation	-----	-----	-----	tres mince	Couche conductrice	----
Environment	L'air, liquide, ...	L'air, liquide	liquide	vide	vide	L'air, liquide

METHODES DE MICROSCOPIE

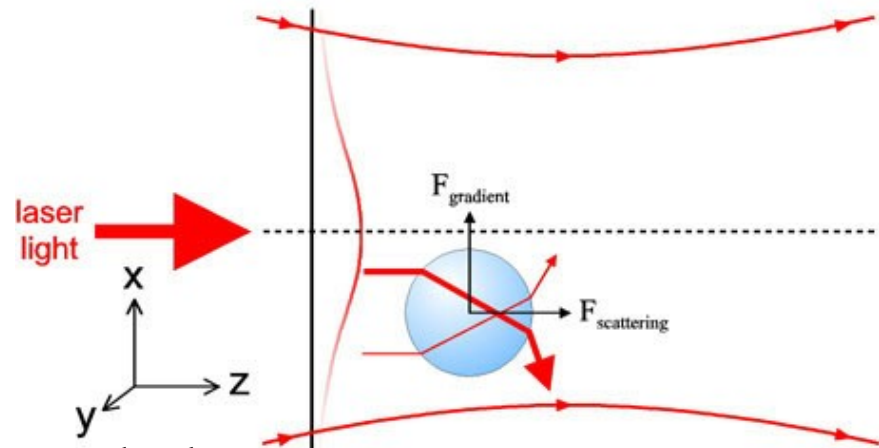
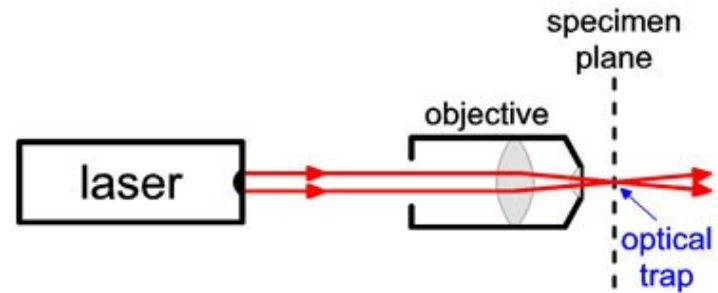
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Optical Tweezers

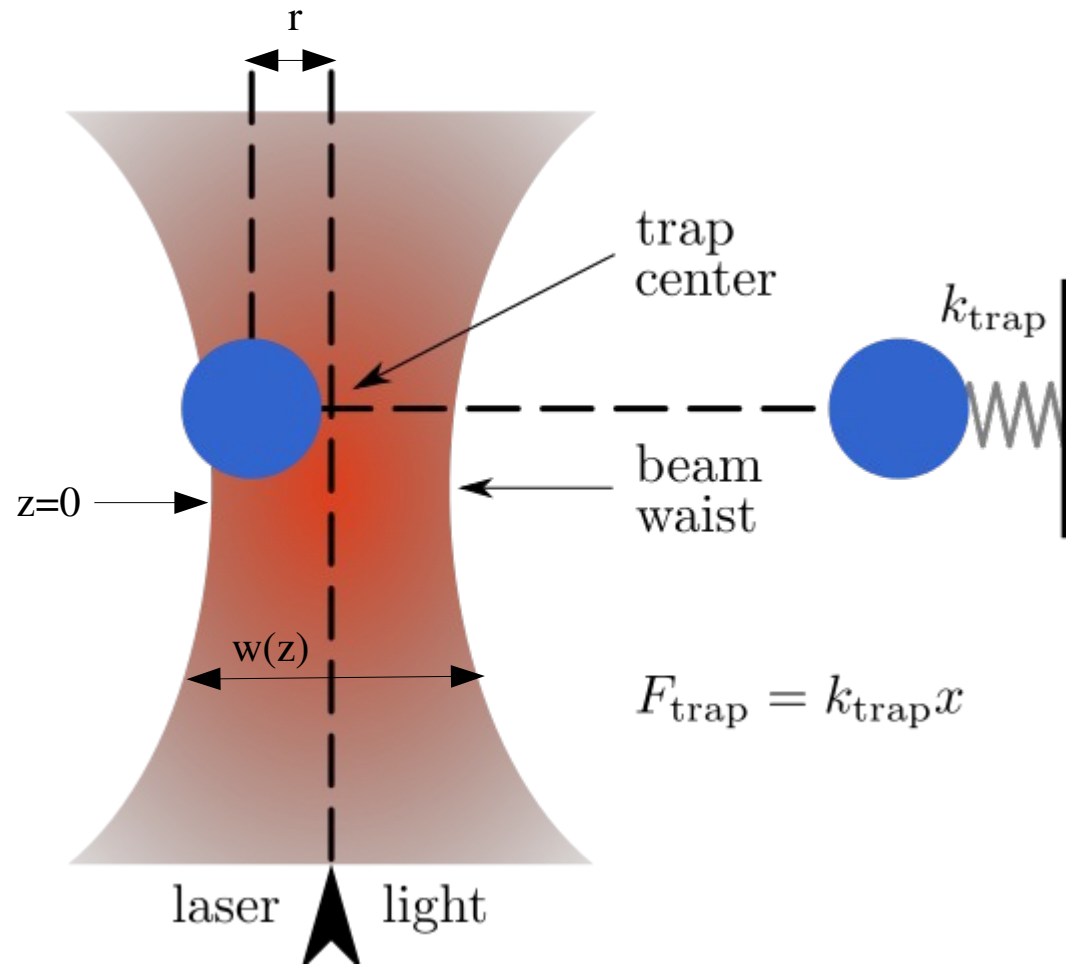
Optical Tweezers use light to manipulate microscopic objects as small as a single atom. The radiation pressure from a focused laser beam is able to trap small particles. In the biological sciences, these instruments have been used to apply forces in the pN-range and to measure displacements in the nm range of objects ranging in size from 10 nm to over 100 nm.

3 regimes:

- $D \gg \lambda \implies$ ray optics
- $D \sim \lambda \implies$ Maxwell's equations
- $D \ll \lambda \implies$ Electrostatics



Optical Tweezers: gaussian beam profile

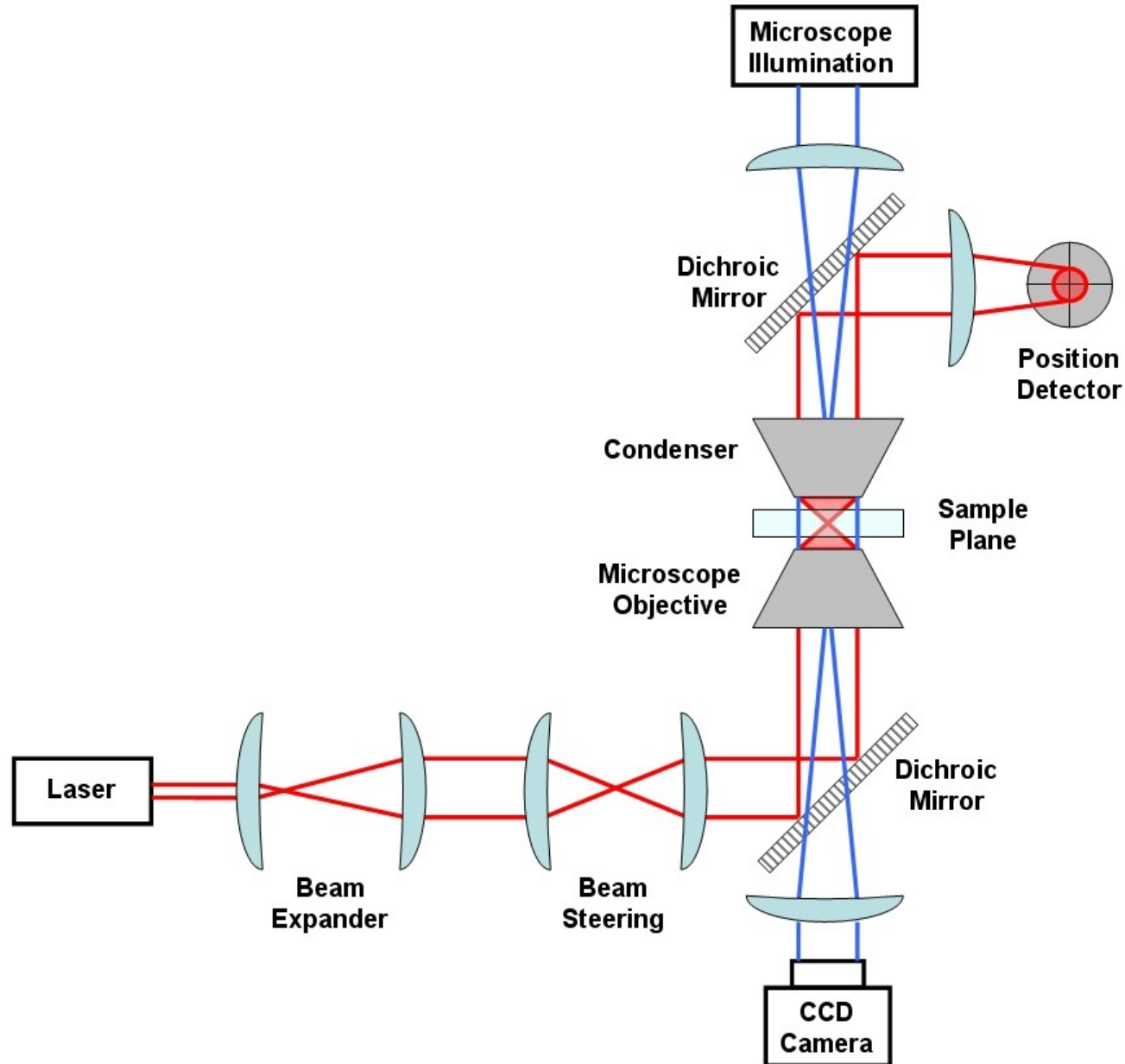


$$I(\mathbf{r}) = \frac{1}{2\eta} E^2(\mathbf{r}) = I_0 \left(\frac{w_0}{w(z)} \right)^2 \exp\left(-\frac{2r^2}{w(z)^2}\right)$$

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}$$

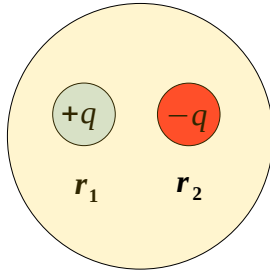
$$z_R = \frac{\pi w_0^2}{\lambda}$$

Optical Tweezers



Optical Tweezers: $D \ll \lambda$

Particle is treated as a point (induced) dipole



$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad \mathbf{d} = q\mathbf{r}$$

$$\mathbf{F}_i = q_i \left\{ \mathbf{E}(\mathbf{r}_i) + \frac{d\mathbf{r}_i}{dt} \times \mathbf{B}(\mathbf{r}_i) \right\}$$

$$\begin{aligned} \mathbf{F}_{total} &= q \left\{ \mathbf{r} \cdot \nabla \mathbf{E}(\mathbf{R}) + \frac{d\mathbf{r}}{dt} \times \mathbf{B}(\mathbf{R}) \right\} + \text{higher order in } r \\ &= \mathbf{d} \cdot \nabla \mathbf{E}(\mathbf{R}) + \frac{d\mathbf{d}}{dt} \times \mathbf{B}(\mathbf{R}) + \text{higher order in } r \end{aligned}$$

Assuming linear dielectric: $\mathbf{d} = \alpha \mathbf{E}$

and using one of Maxwell's equations: $\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$

$$\mathbf{F}_{total} = \alpha \left\{ \nabla E(\mathbf{R})^2 + \frac{\partial}{\partial t} \underbrace{(\mathbf{E}(\mathbf{R}) \times \mathbf{B}(\mathbf{R}))}_{\text{power per unit area}} \right\} + \text{higher order in } r$$

For dielectric sphere

$$\begin{aligned} \alpha &= \frac{\pi D^3 \epsilon_0}{2} \frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} \\ &\approx \frac{\pi D^3 \epsilon_0}{2} \frac{n^2 - n_0^2}{n^2 + 2n_0^2} \end{aligned}$$

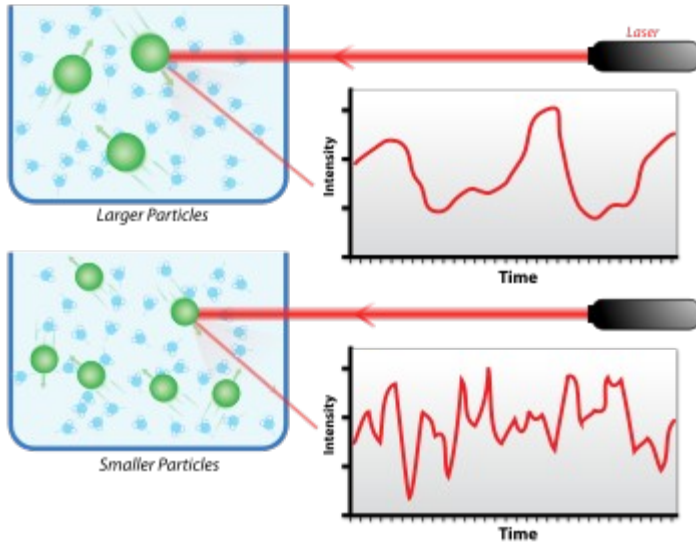
Proof = exercise!

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Dynamic light scattering

- Typically used for particles diffusing in a liquid bath
- Determines size of particles



Field auto-correlation function (what you want):

$$g_1(q, t) = \frac{\langle E(q, t) E(q, t + \tau) \rangle}{\langle E(q, t) E(q, t) \rangle}$$

$$g_1(q, t) = \exp(-q^2 D t), \quad D = \text{diffusion constant}$$

$$q = \frac{4 \pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

$$D = \frac{k_B T}{6 \pi \eta R}$$

← Radius of particles

(Stokes-Einstein relation)

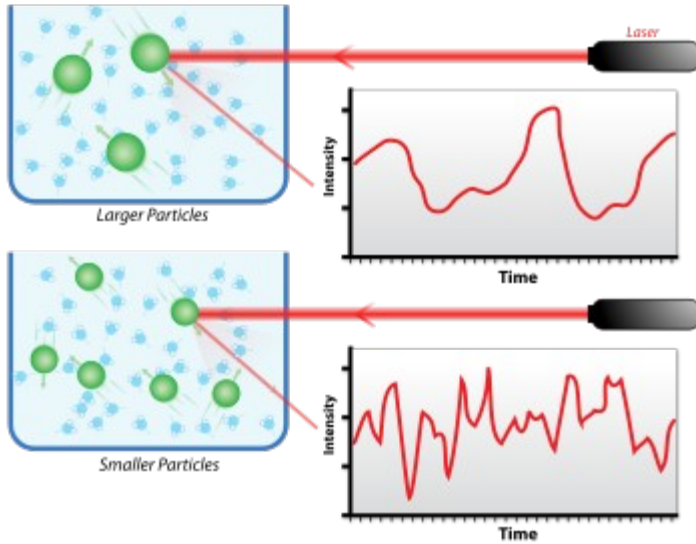
Intensity auto-correlation function (what you measure):

$$g_2(q, t) = \frac{\langle I(q, t) I(q, t + \tau) \rangle}{\langle I(q, t) I(q, t) \rangle}$$

$$g_2(q, t) \sim 1 + \text{const} \times [g_1(q, t)]^2$$

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