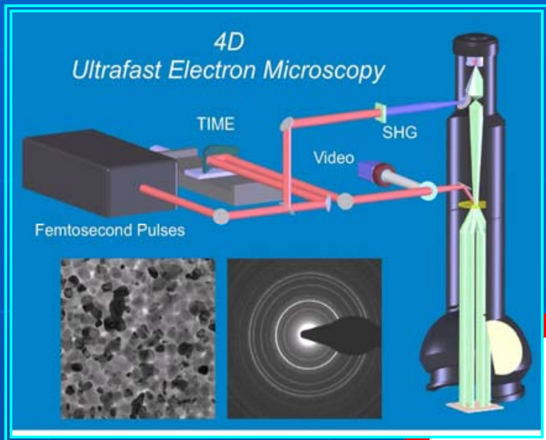
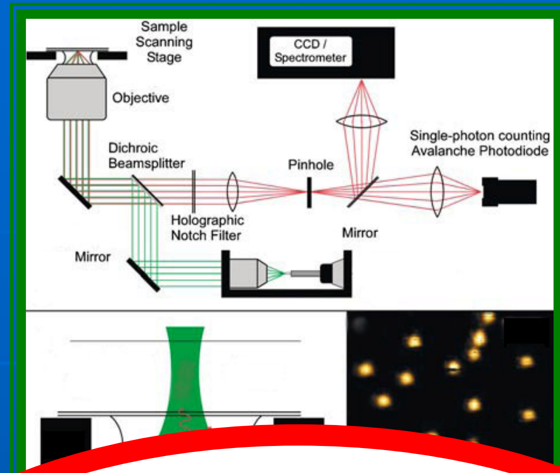
Studies of light-induced stochastic and coherent processes in nano-structured materials using single-molecule techniques and femtosecond time-resolved electron diffraction

Jau Tang 湯朝暉

Research Center for Applied Sciences,
Academia Sinica, Nankang, Taiwan
and
Department of Photonics
NCTU, Hsinchu, Taiwan





Quantum dots, Nanorods,
Biomolecues,
Metallic & Semiconductor films & NCs
Organic conductors, photovoltaics
Light-induced phase transitions

Structure
Dynamics
Functionality

Outline

Time-resolved electron diffraction and microscopy

Impulse-induced structural dynamics & its effects on diffraction patterns

Coherent acoustic wave excitation

Nano-scale heat transfer of laser-heated metals

Light-induced insulator-metal phase transitions

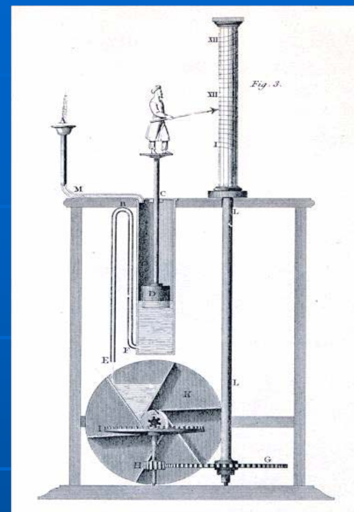
Confocal microscopy and single-molecule techniques

Fluorescence intermittency of illuminated nano-particles

Photo-induced charge transfer

Enzymatic reactions and intermittency of single biomolecules

Förster's fluorescence resonance energy transfer water clock (1500 BC)



Egyptian water clock (300 BC)

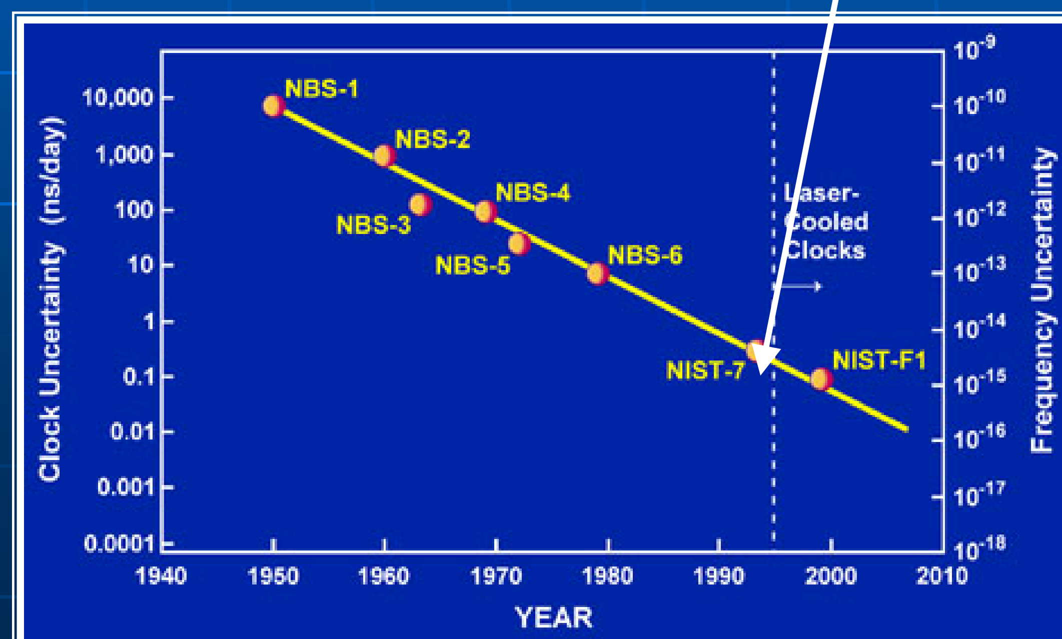
NIST F-1, (cesium fountain clock)

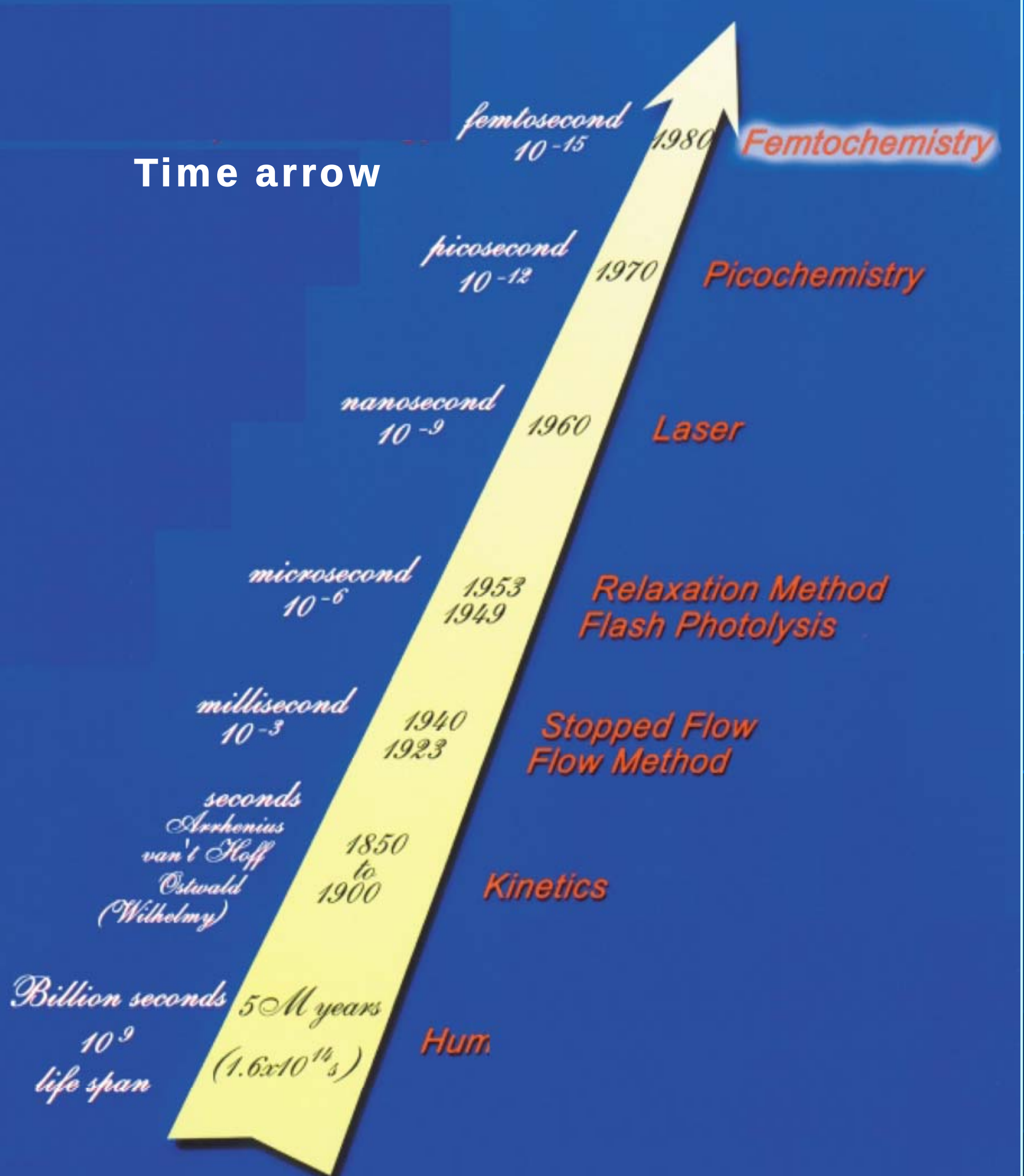
NIST F-1 Atomic Clock

accuracy: 10^{-15}

Sun dial clock (300 BC)

Pendulum clock (1500 AD)





Maser – 1954

CW Laser – 1959

Nanosecond laser – 1960s

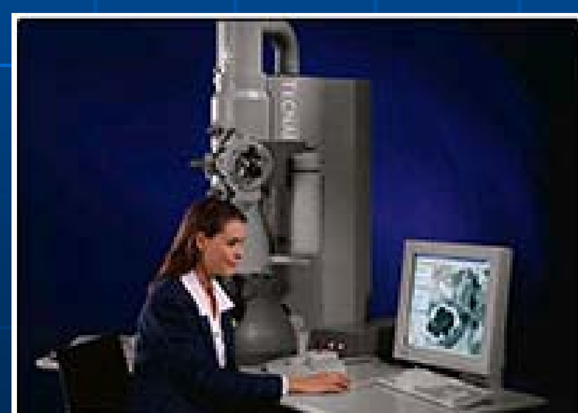
Picosecond laser – 1970s

Femtosecond laser – 1980s

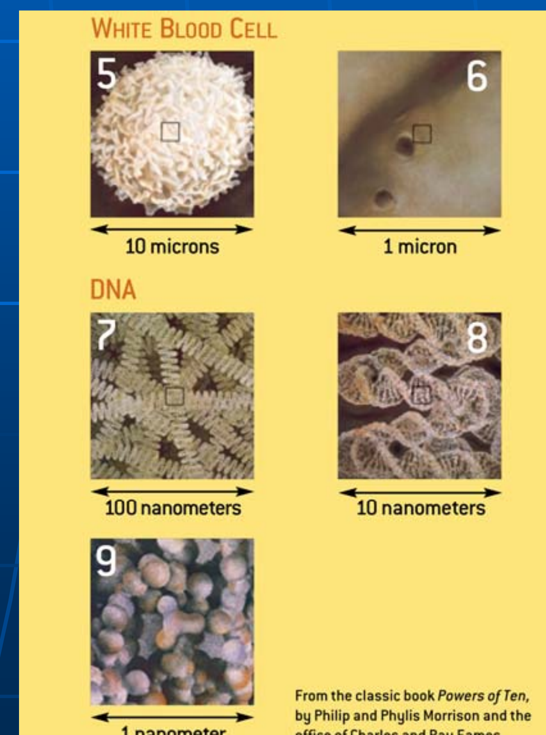
A macro, micro and nano view of a human hand, 10 times magnification per frame.

(magnifying glasses invented 1st century)

Janssen, Leeuwenhoek (16th century)



Knott, Ruska (1930)



maximum theoretical resolution
~ l/2 wavelength

radios ~ miles to mm
infrared ~ mm to 800nm
light ~ 400-800nm
electrons ~ 20kV 0.008 nm

under the best of conditions:

human eye	~ 0.2 mm
light scope	~ 0.2 um
SEM	~ 3 nm
TEM	~ 0.2 nm

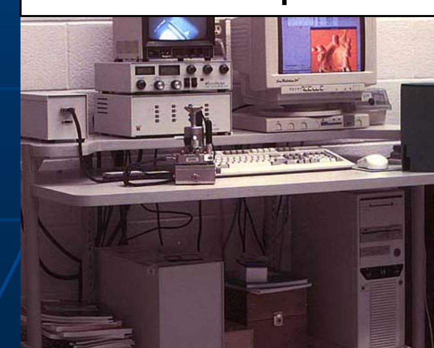
- Electron Microscopes were not developed until the Twentieth Century
- The first Transmission Electron Microscope (TEM) was built in 1932
- The first Scanning Electron Microscope (SEM) was built in 1942.
- The Scanning Tunnelling Microscope was developed in 1982.
- The Atomic Force Microscope was developed in 1985.

Transmission Electron Microscope

Scanning Electron Microscope

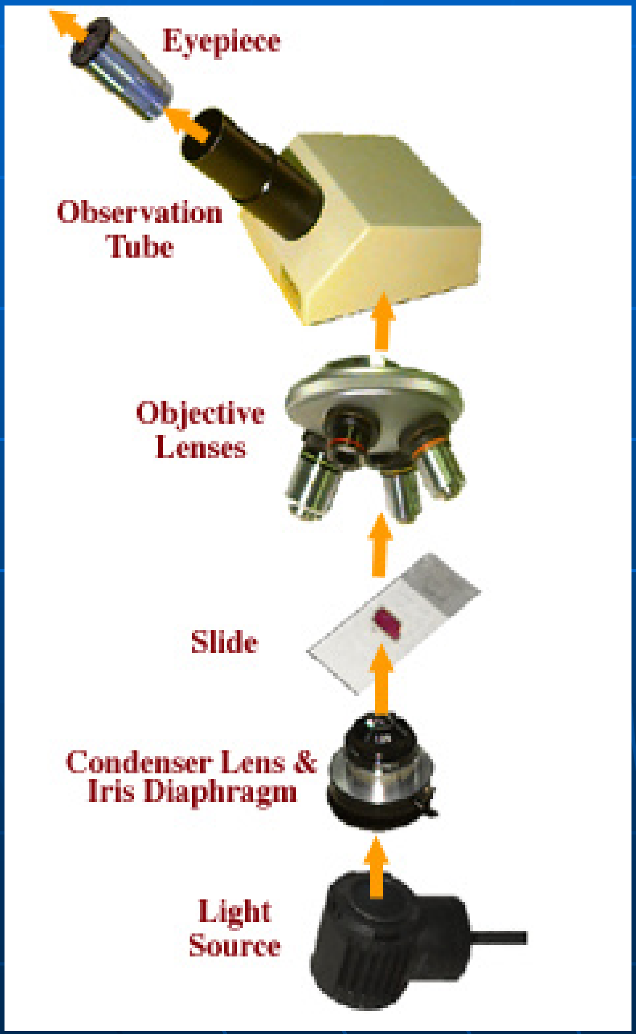
Scanning Tunneling Microscope

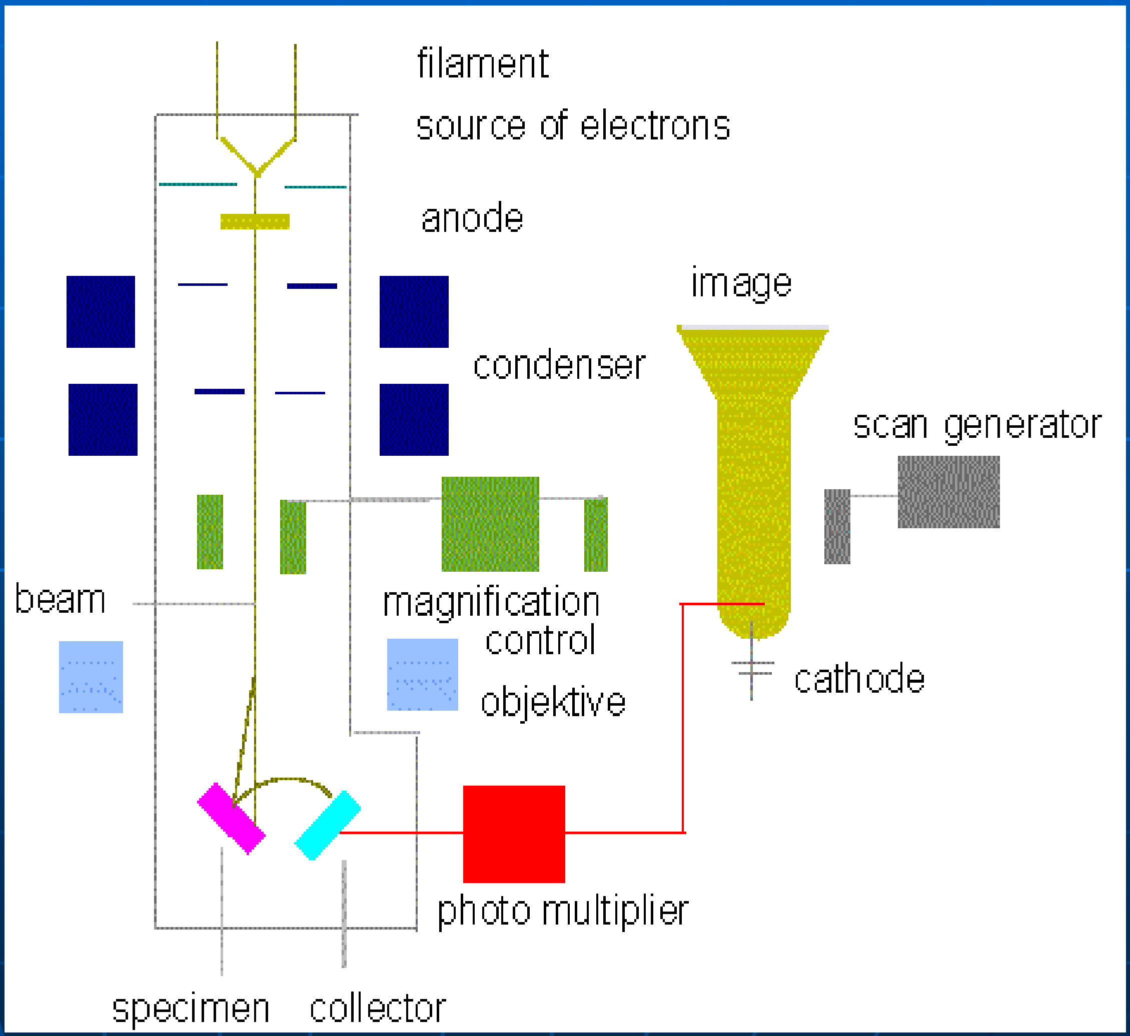
Atomic Force Microscope

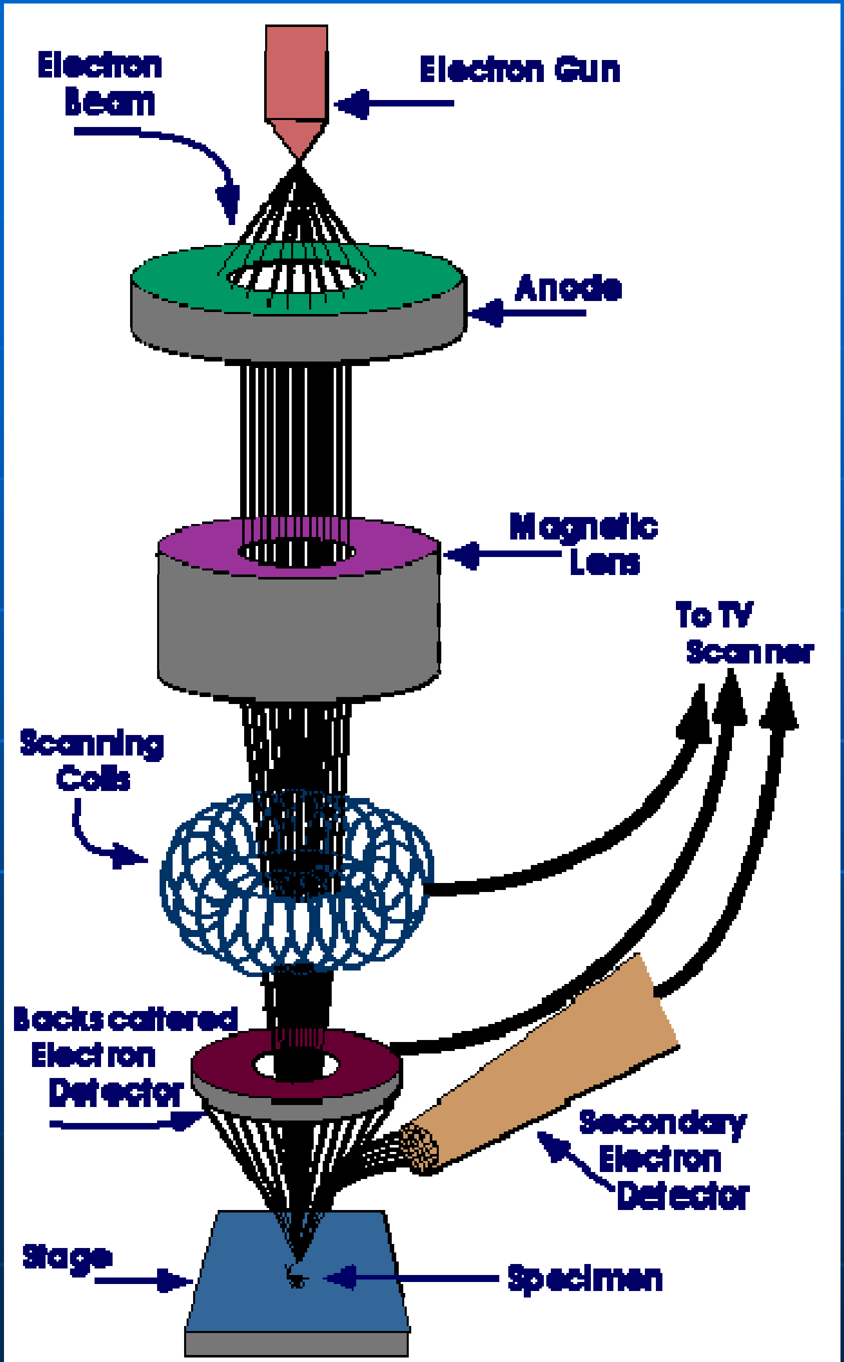


- Electrons can be focussed using magnetic lenses
- Shorter wavelength than visible light

SEM





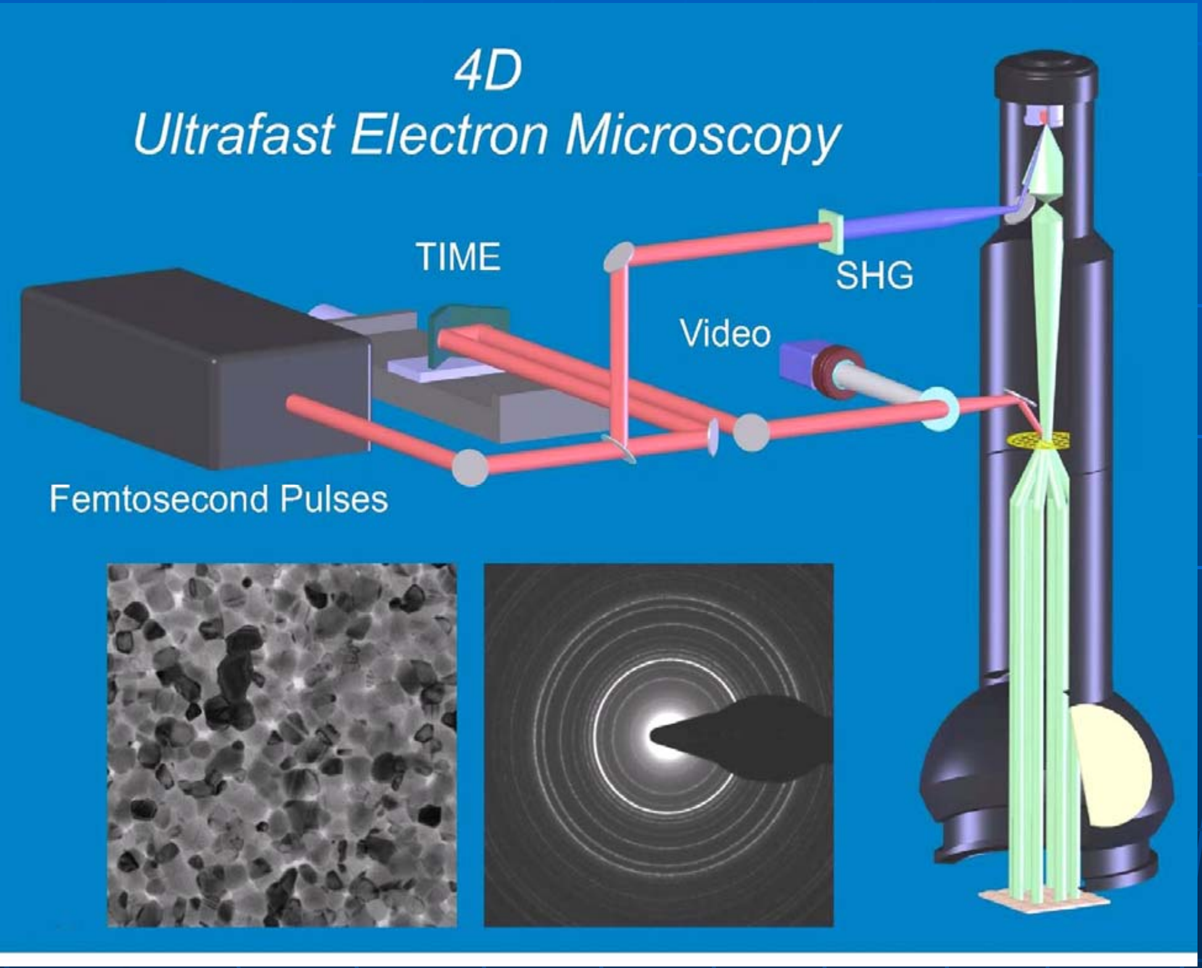


SEM

- Large depth of field
  More of the sample is in focus at one time
- Higher resolution
  Smaller features can be imaged
- Analysis
  The electron beam interacts with the sample enabling information on composition to be collected using additional detectors

Studies of structural dynamics by

Ultrafast Electron Diffraction and Microscopy



nm spatial resolution

fs time resolution

Electron gun cathode
Lanthanum Hexaboride
LaB_6

Low work function ~ 2.5 eV

Melting pt.: 2530 ℃

pulsed X-ray diffraction

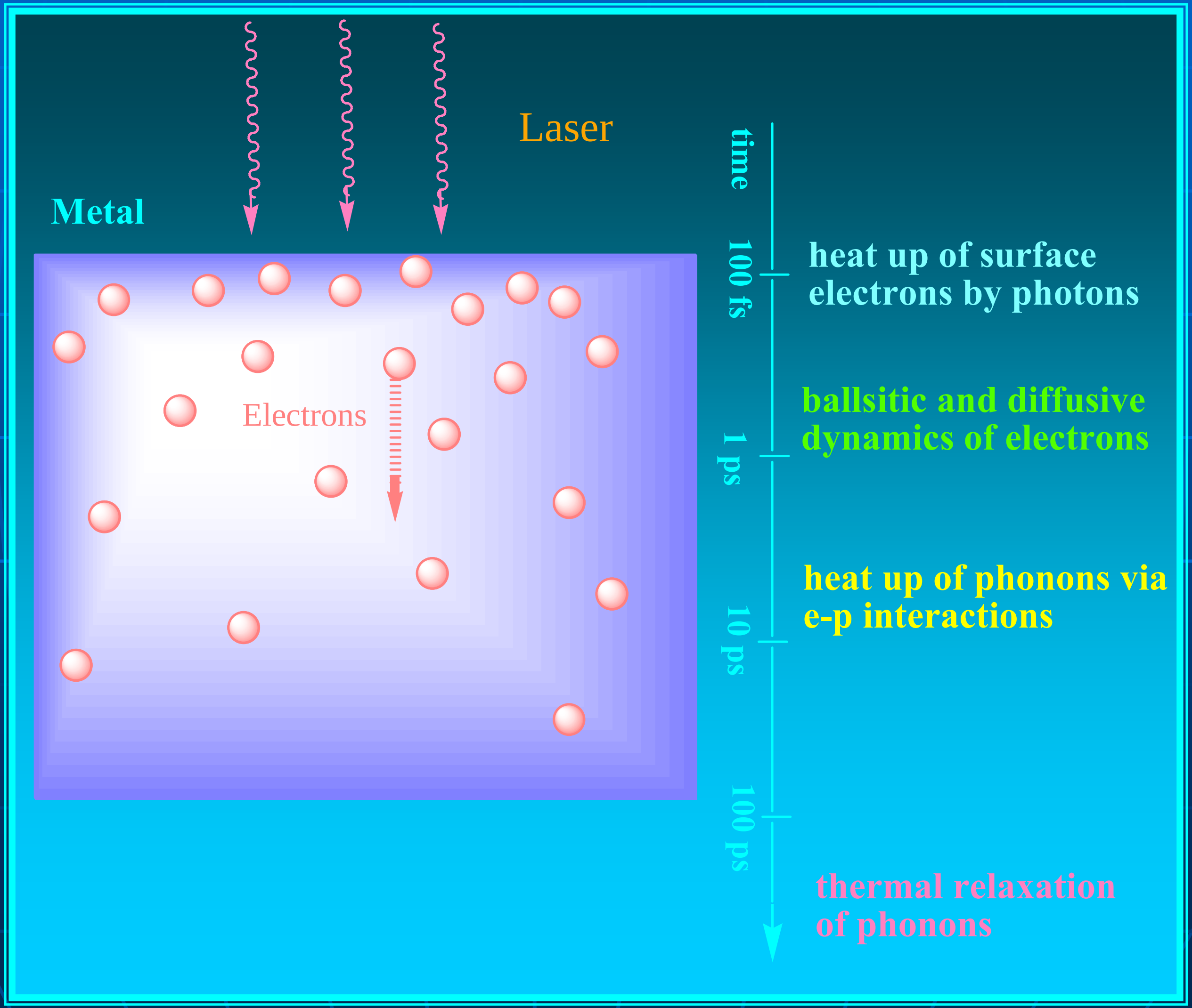
- Hugh synchrotron
- Small scatter cross section
- Deep penetration depth
- Thick and large sample
- Bulk materials

pulsed electron diffraction

- Desk top operation
- Larger (10^6) scatter cross section
- Shallow penetration depth
- Thin and small samples
- nano-structured materials and surface science

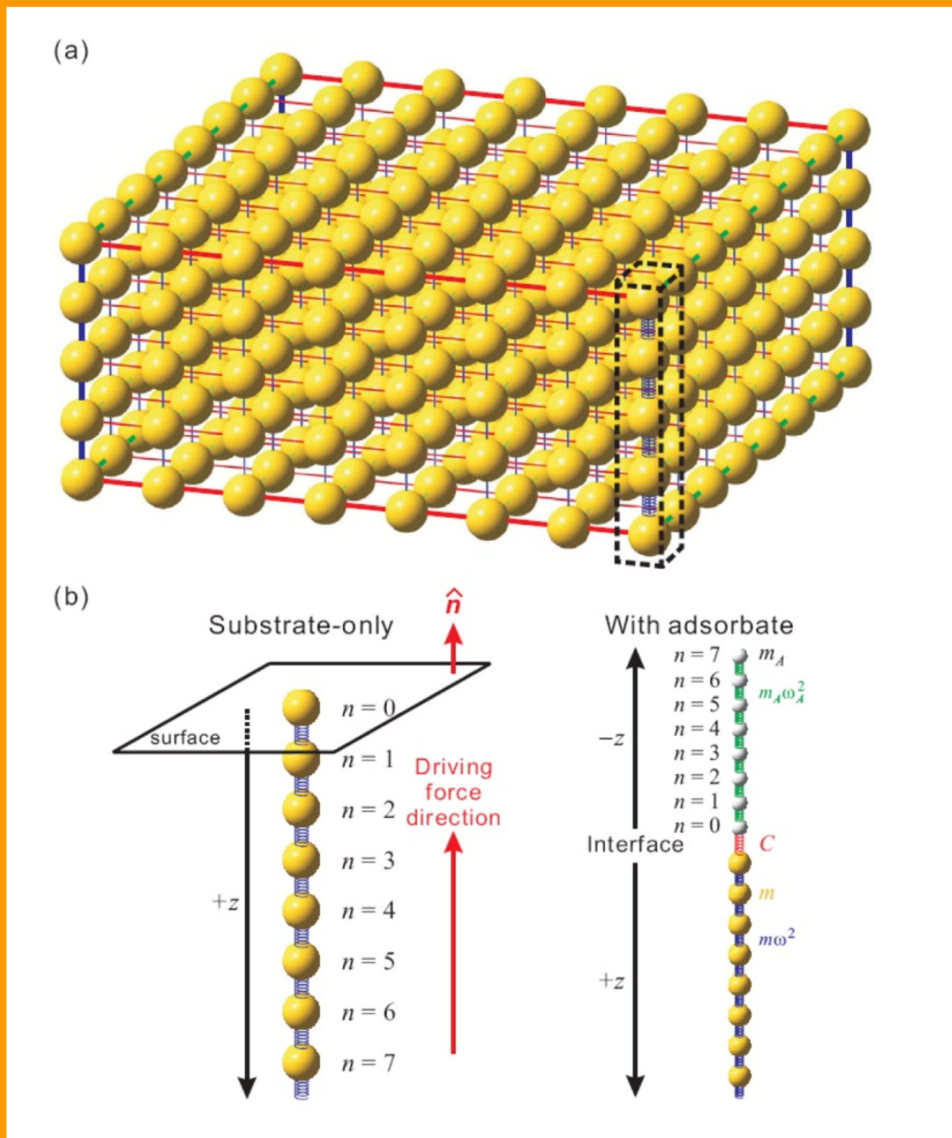
Ultrafast Electron Crystallography of Laser Heated Metals

J. Tang, D.-S. Yang and A. H. Zewail, J. Phys. Chem. C, (2007)

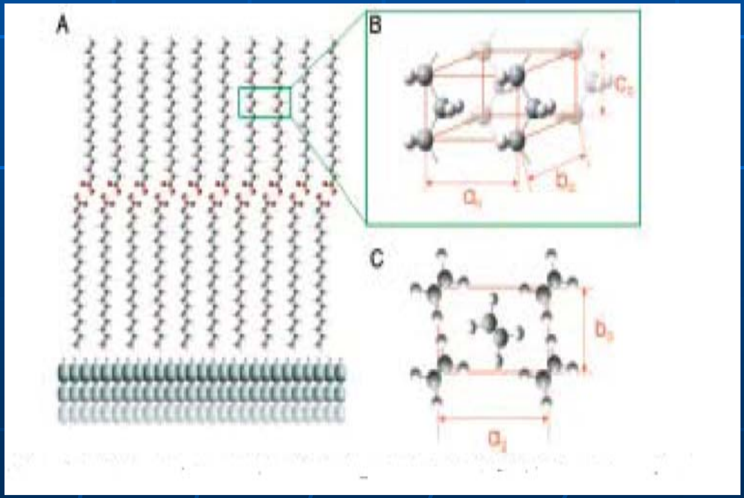


Fermi-Pasta-Ulam model

Anharmonic chain

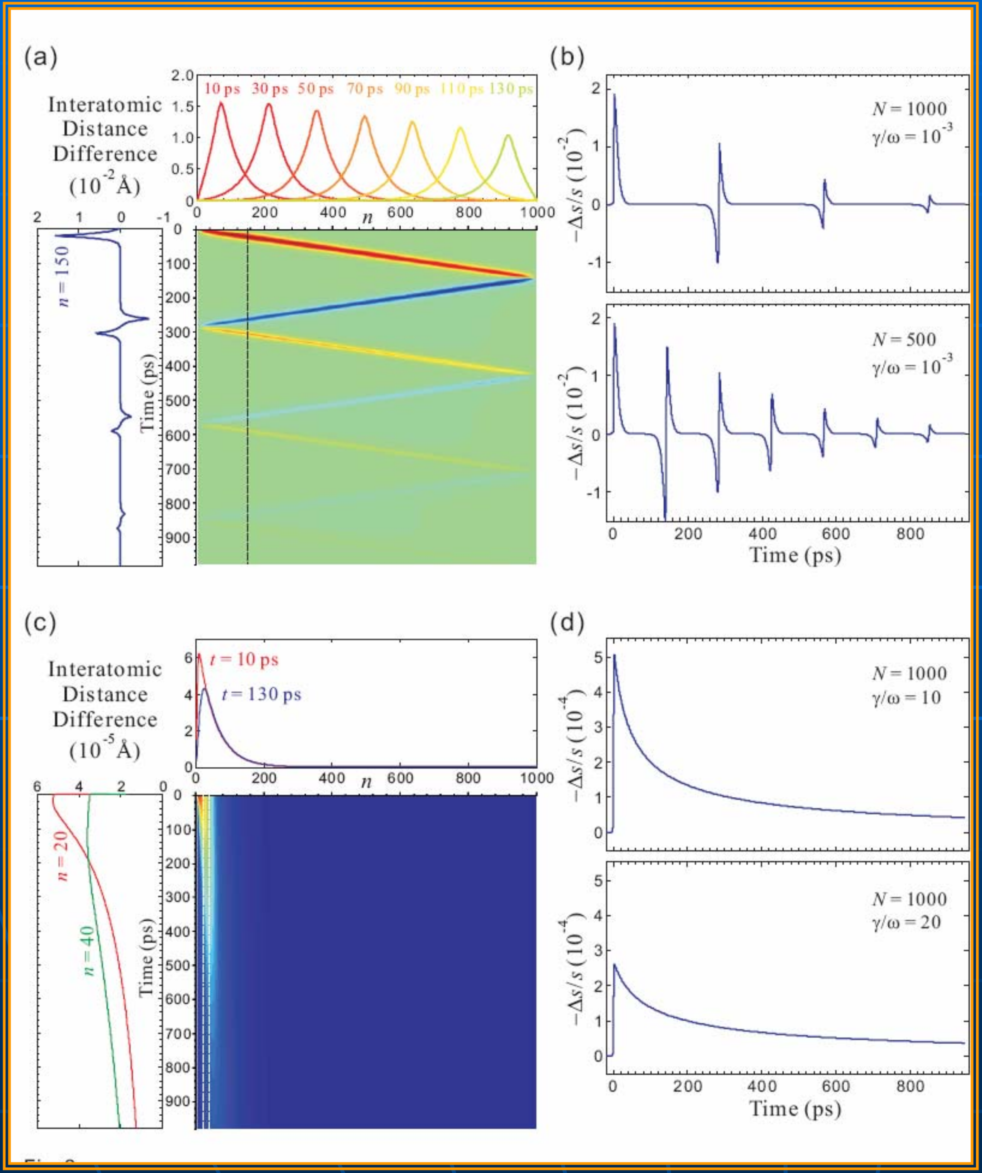


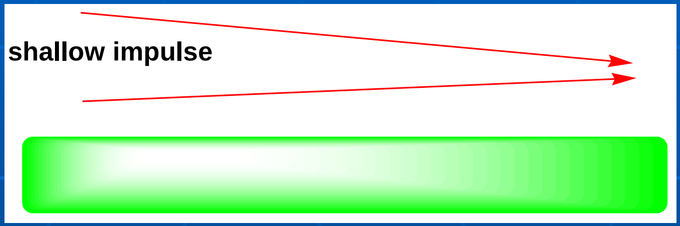
$$H=\sum_{k=0}^{N-1}\frac{p_k^2}{2m_k}+\sum_{k=0}^{N-2}\frac{m_k\,\omega_k^2}{2}\left(q_k-q_{k+1}\right)^2+\sum_{k=0}^{N-2}\alpha_k\frac{m_k\,\omega_k^2}{3}\left(q_k-q_{k+1}\right)^3$$



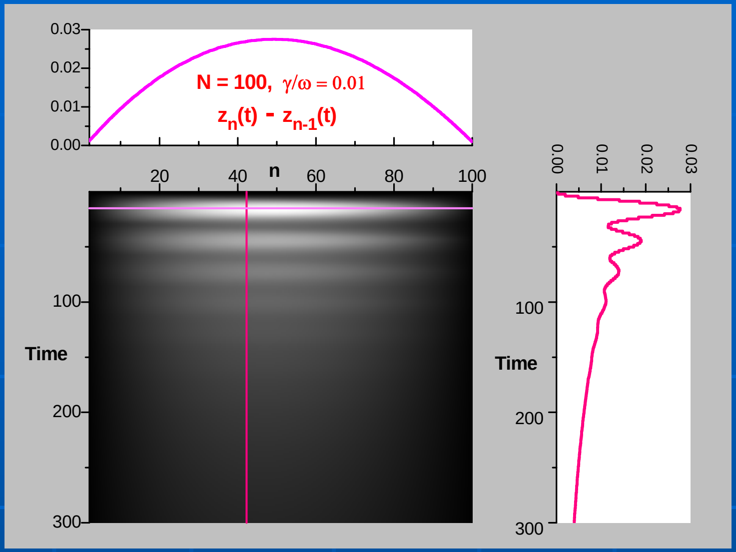
UEC of Gold Film

Shallow impulse, N = 1000





Inter-atomic spacing



UEC of a thin gold film

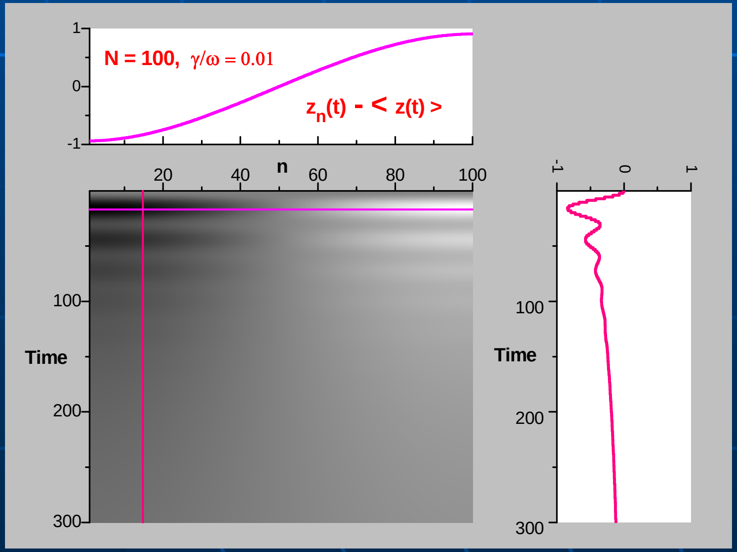
N = 100

Deep impulse

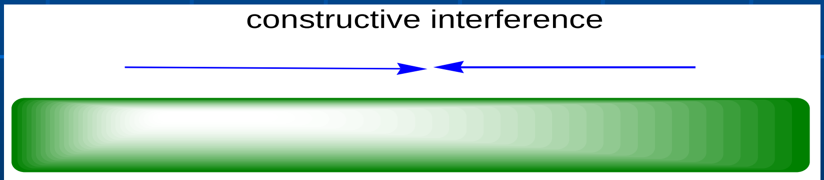
“breathing” phenomenon

Wavelength / 2 = slab thickness
Period / 2 = thickness / sound speed

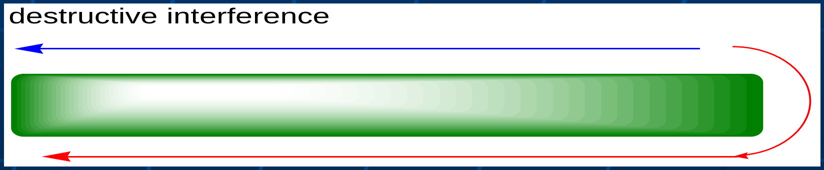
Position shift w.r.t. center of mass



Largest expansion in the middle

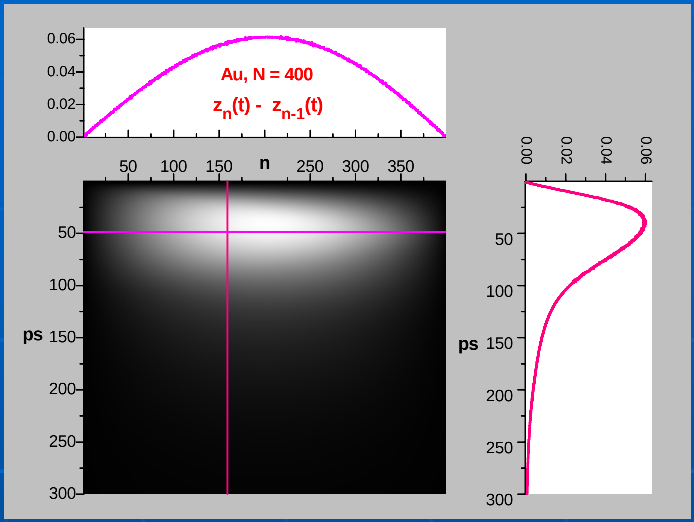


Smallest expansion on both surfaces

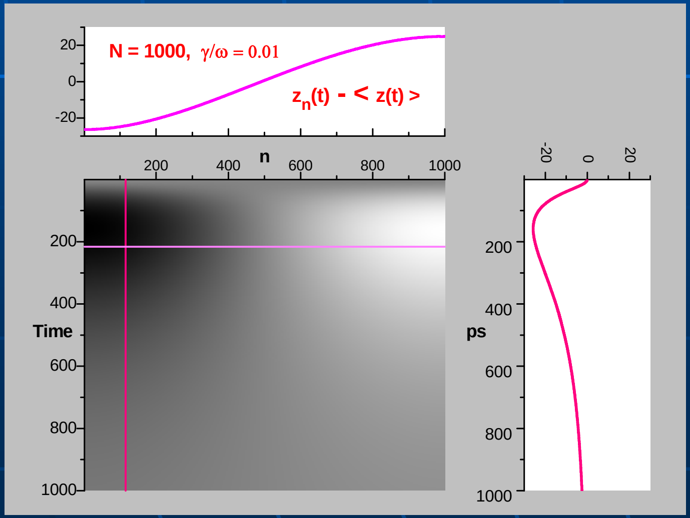


UEC of Gold Film N = 400

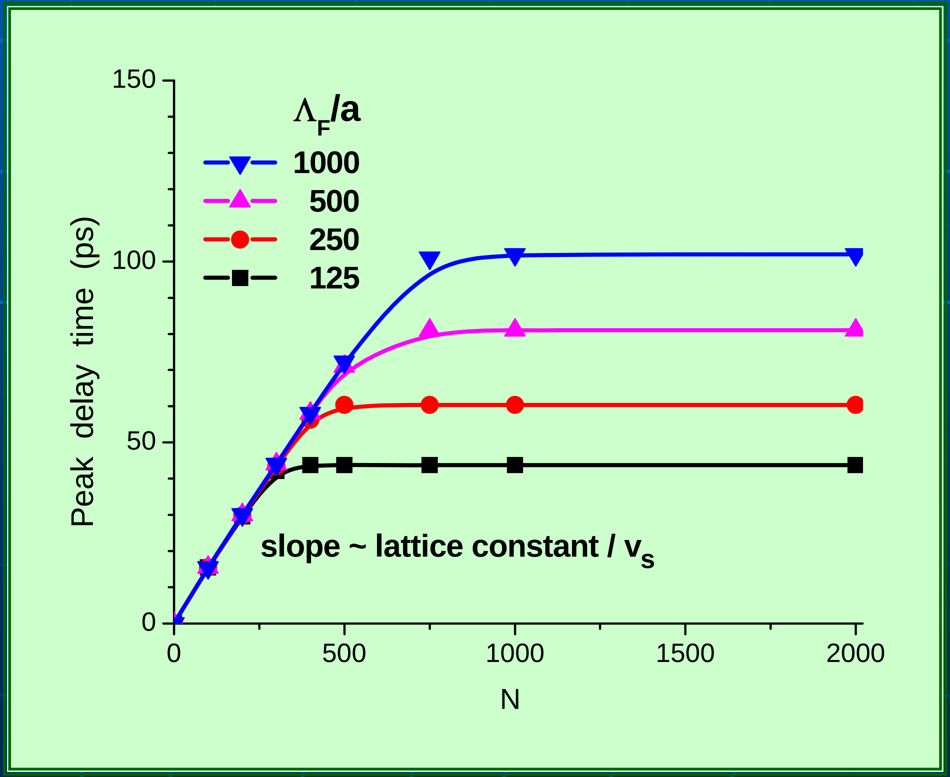
Inter-atomic spacing



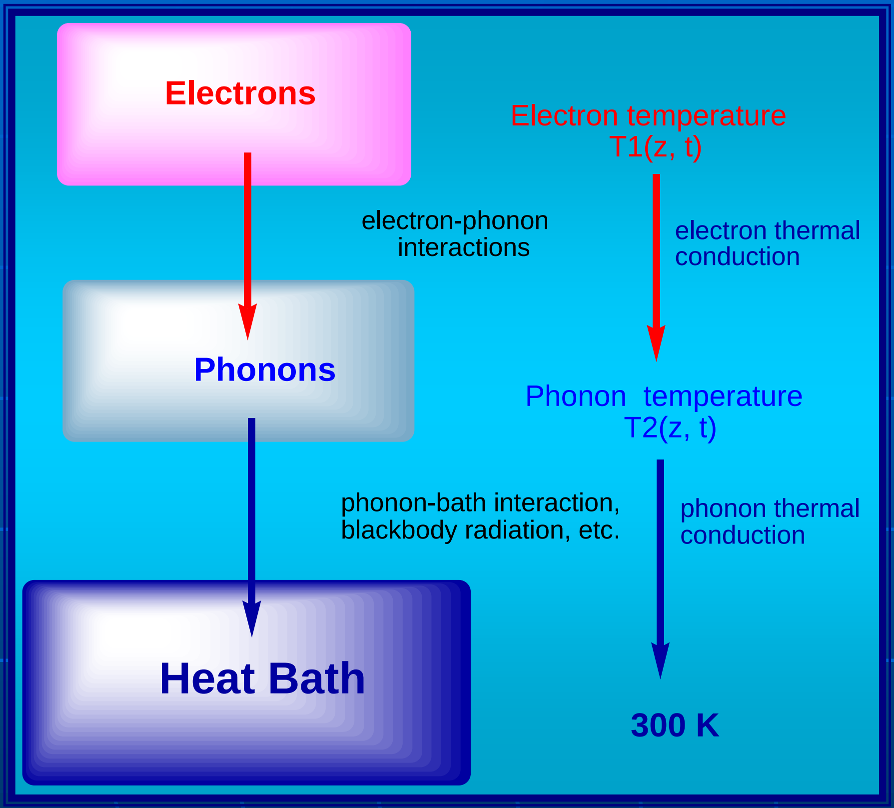
Position shift w.r.t. center of mass



Dependence of the peak delay time on the thickness of a substrate



Laser heating of metals and two-temperature model



$$\frac{\partial}{\partial t}[C_e(T_1)T_1(z,t)] = \frac{\partial}{\partial z}\left(\kappa_e(T_1)\frac{\partial}{\partial z}T_1(z,t)\right) - g(T_1(z,t) - T_2(z,t)) + S(z,t)$$

$$C_2\frac{\partial}{\partial t}T_2(z,t) = \kappa_L\frac{\partial^2}{\partial z^2}T_2(z,t) - g(T_2(z,t) - T_1(z,t))$$

Temperature-induced impulsive forces

$$F_k(t) = -\gamma_{2,G}C_2\left(T_{2,k}(t) - T_0\right)\ell^2 - \gamma_{1,G}C_1T_{1,k}(t)\left(T_{1,k}(t) - T_0\right)\ell^2$$

Spatial and temporal dependence of electron and phonon temperatures → **Impulsive force on each atom** → **Transient atomic Displacement & Bragg peak shift**

$$\textit{Aluminum}: \quad \gamma_{2,G} \sim 2.2 \quad \textit{phonons}$$
$$\gamma_{1,G} \sim 1.6 \quad \textit{electrons}$$

Heat capacity of electrons ~ T

Fermi electron gas model

$$C_e(T) \sim (\pi^2 N k_B / 3T_F)\, T\,, \qquad T_F = E_F / k_B$$

Fermi temperature: Au - 6.4 x 10^4, Al - 13.6 x 10^4, Cu - 8.2 x 10^4

Heat capacity of phonons ~ constant in T

$$C = \frac{\partial}{\partial T} \sum_{k,} \frac{\hbar\omega_k}{\exp(\hbar\omega_k / k_B T) - 1} \approx 3N_A k_B$$

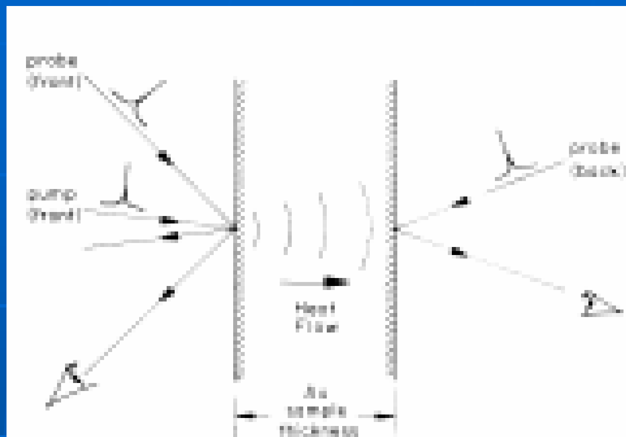
Dulong-Petit value

Electronic thermal conductivity ~ T

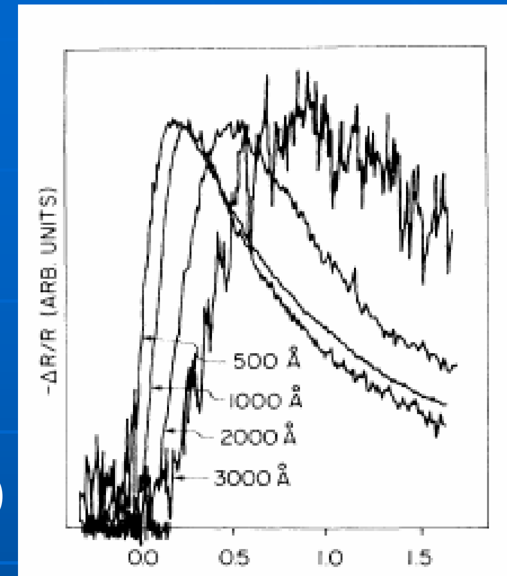
$$\kappa_e = \frac{\pi^2 k_B^2 n_e \tau}{3m_e} T\,, \quad \tau \;\; scattering\ relaxation\ time$$

$$\Lambda = v_F\,\tau \quad mean\ free\ path$$

Transient optical reflectivity of a gold film



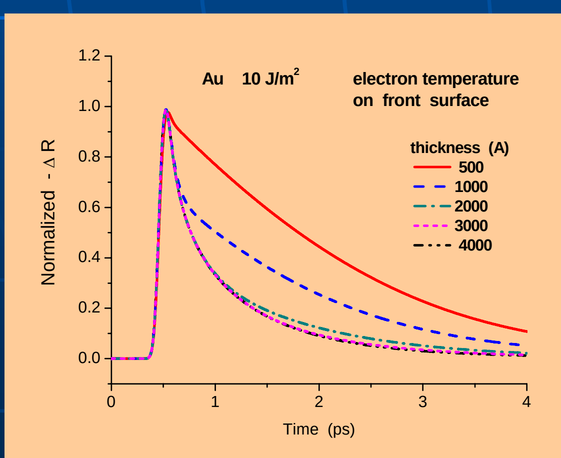
(rear surface)

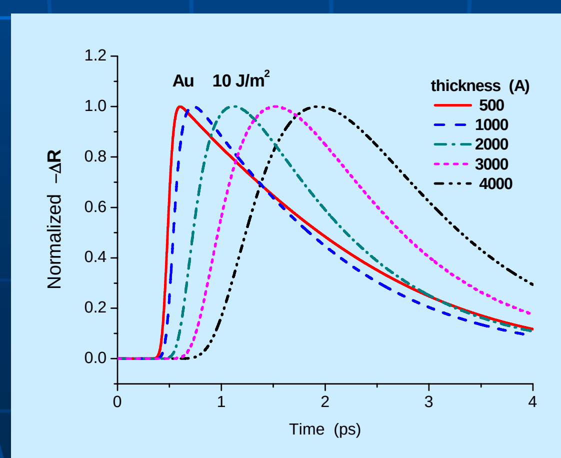


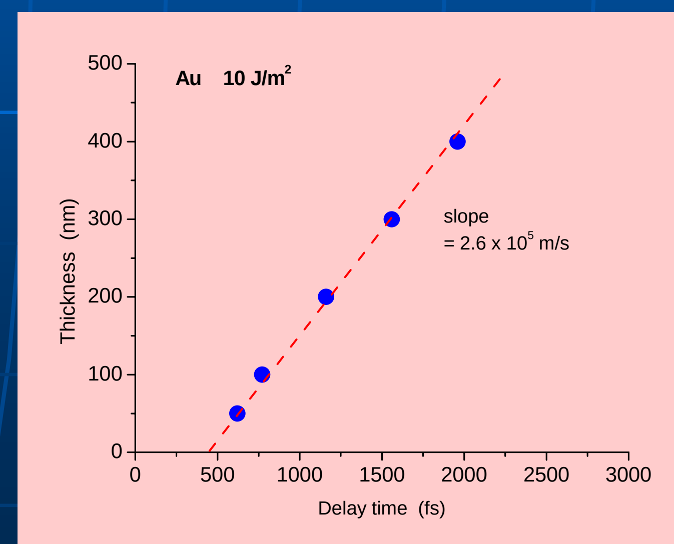
E. P. Ippen et al. Phys. Rev. Lett. 59, 1962, (1987)

Supersonic hot electrons

TTM (front surface) (rear surface)

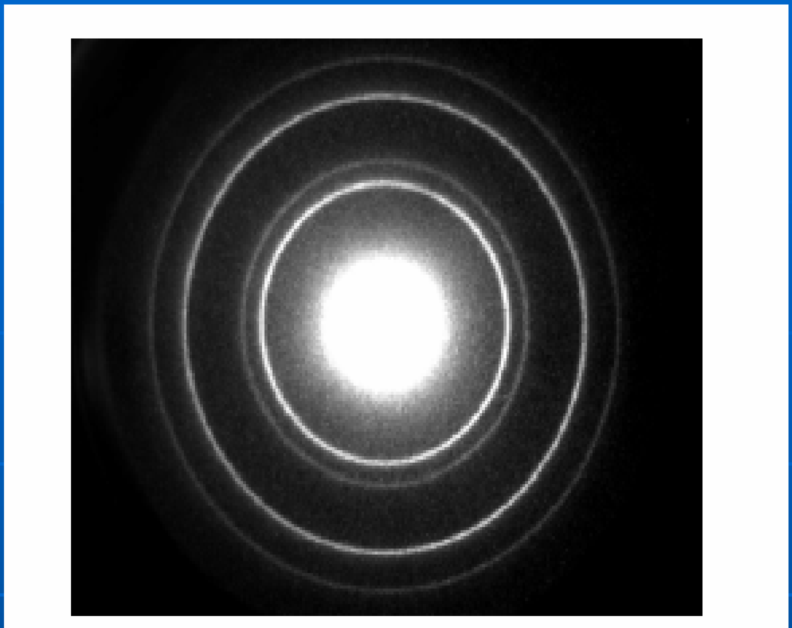


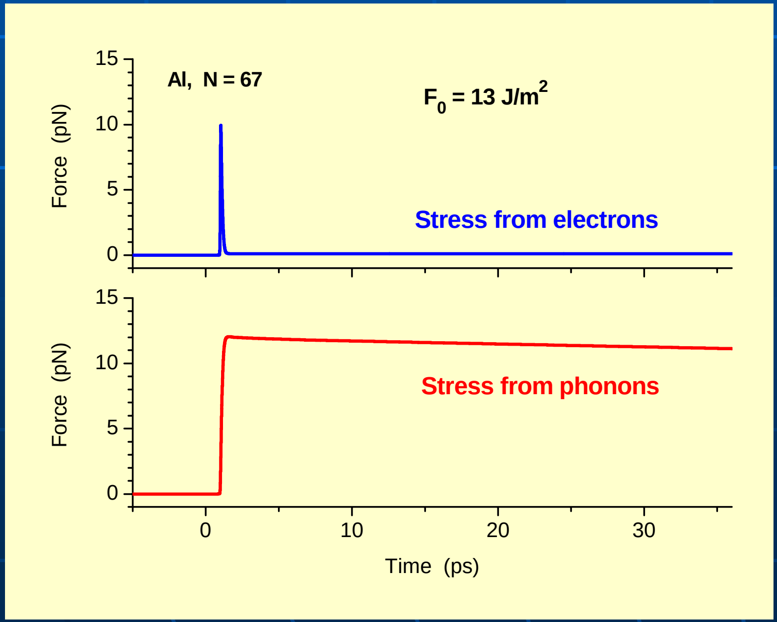




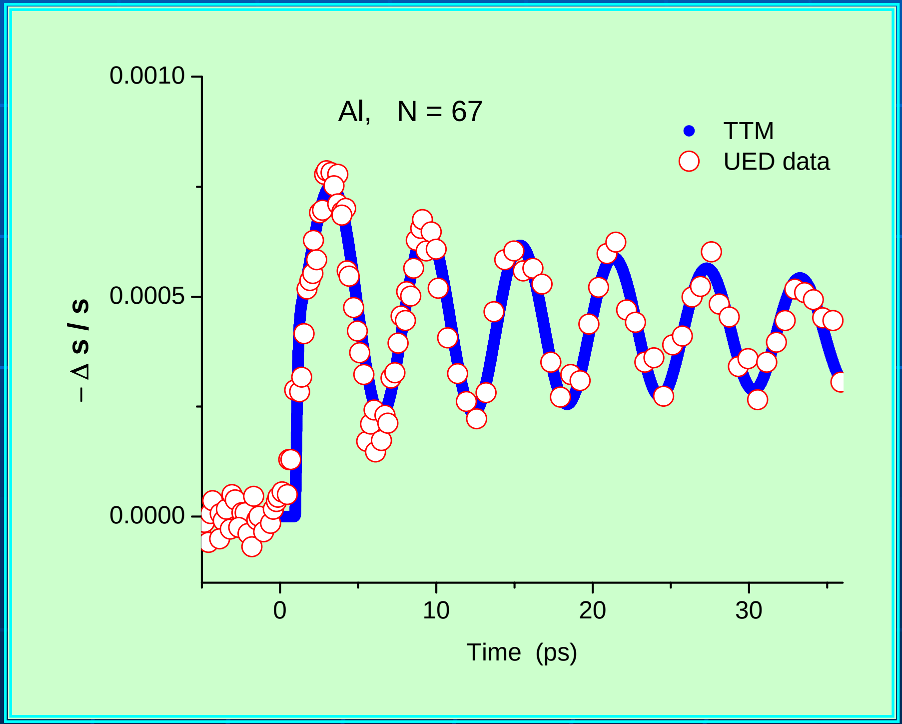
UEC of Aluminum Film

J. Cao et al. Phys Rev. Lett. (2006)
(20 nm thickness, fluence 13 J/m^2)





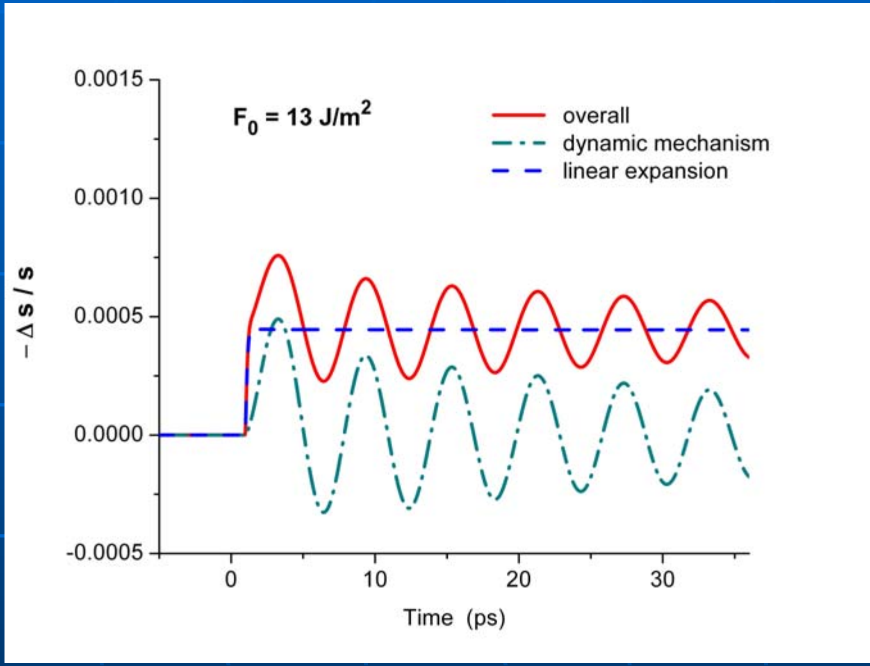
Acoustic wave excitation



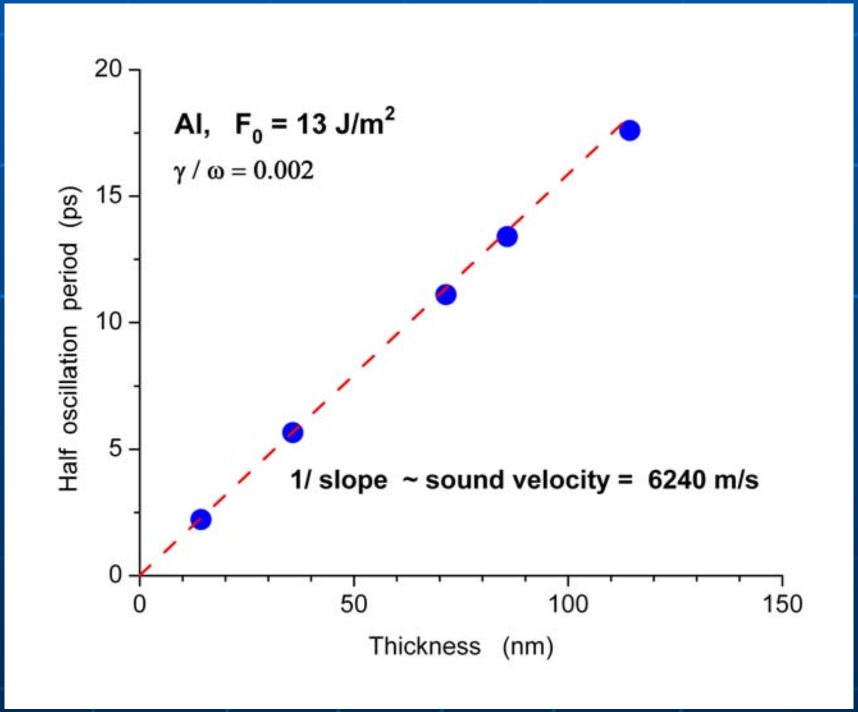
J. Tang, PRL (submitted)

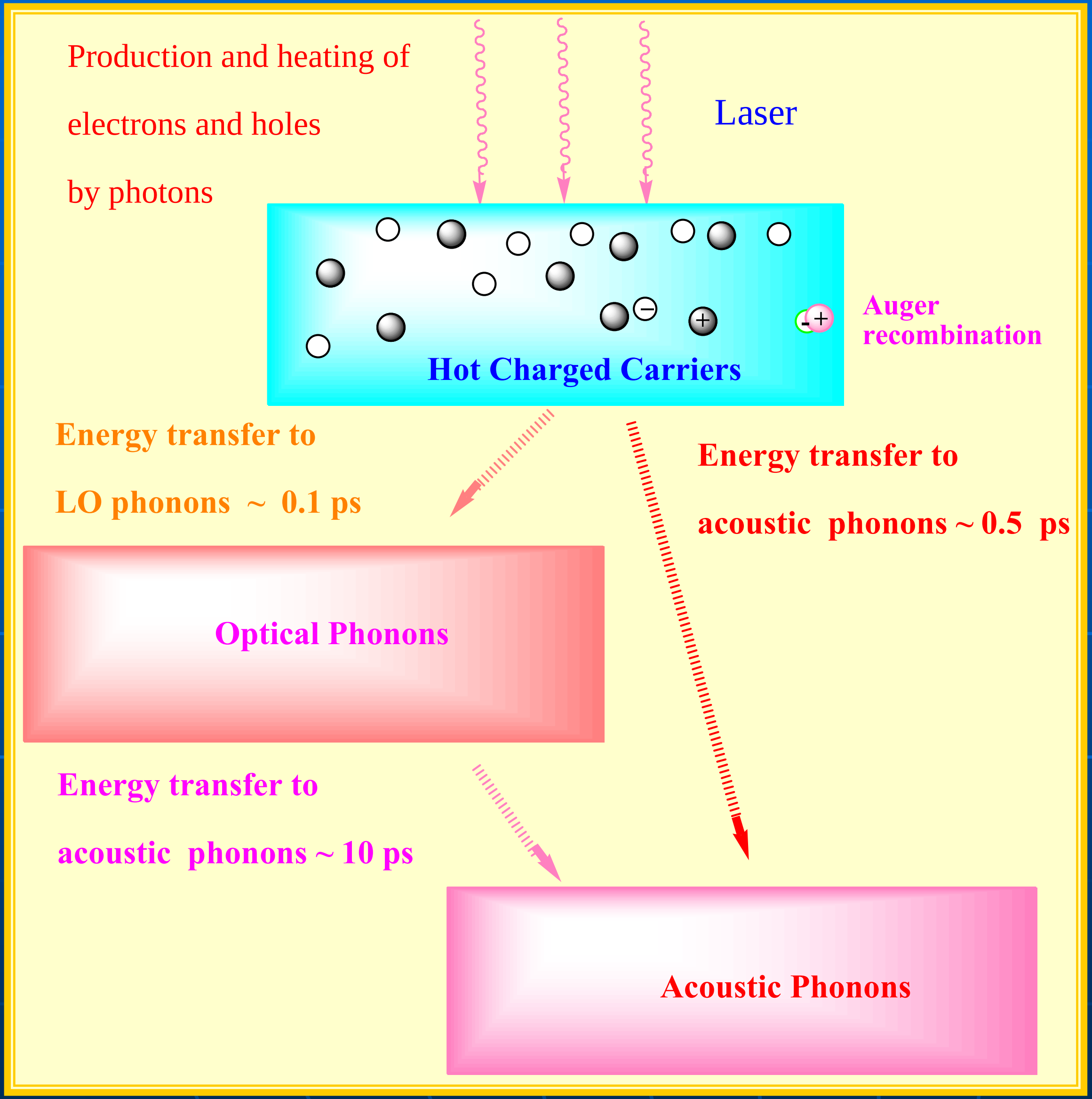
Dynamic mechanism

Static linear thermal expansion



Half oscillation period vs. thickness





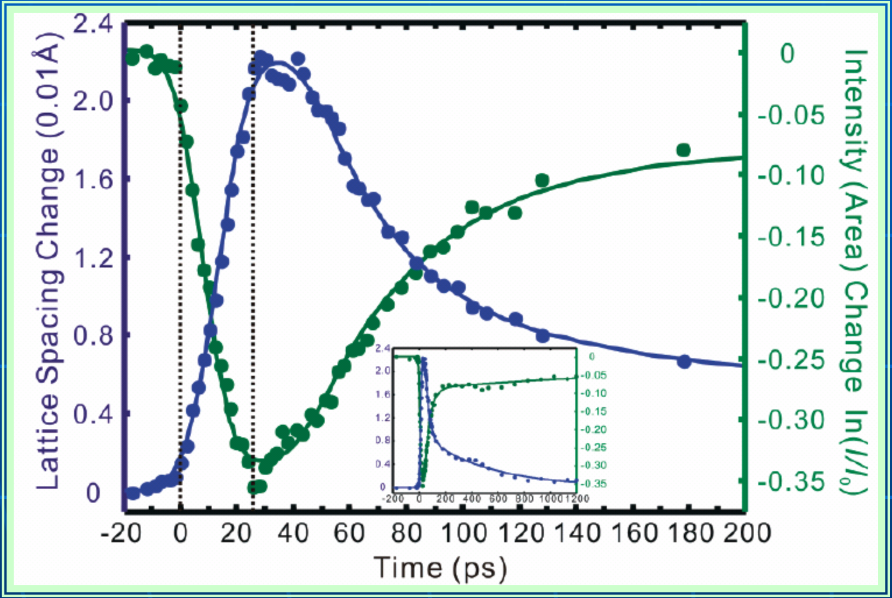
Laser heating of Si & GaAs semiconductors and three-temperature model

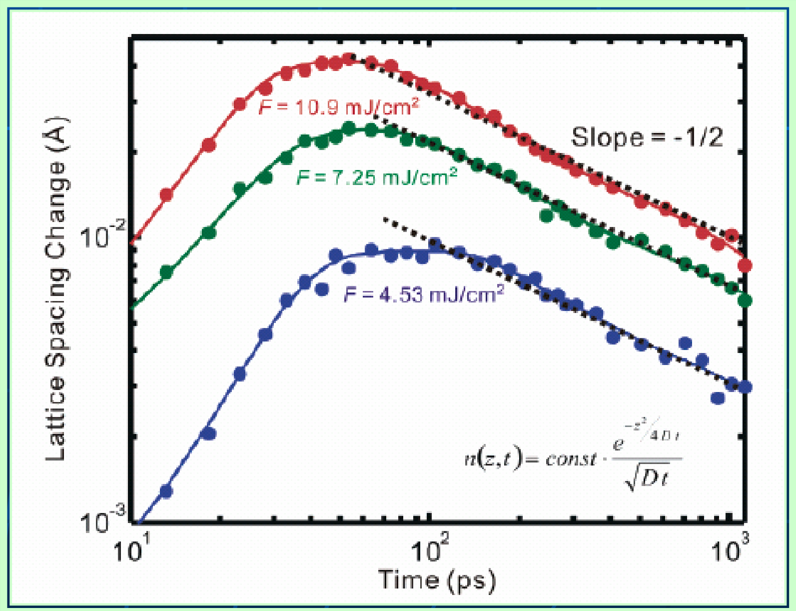
Charged carriers

Optical phonons

Acoustic phonons

UEC of GaAs thin film





Yang, Gedik and Zewail, JPC (2007)

Dynamic vs. static mechanisms

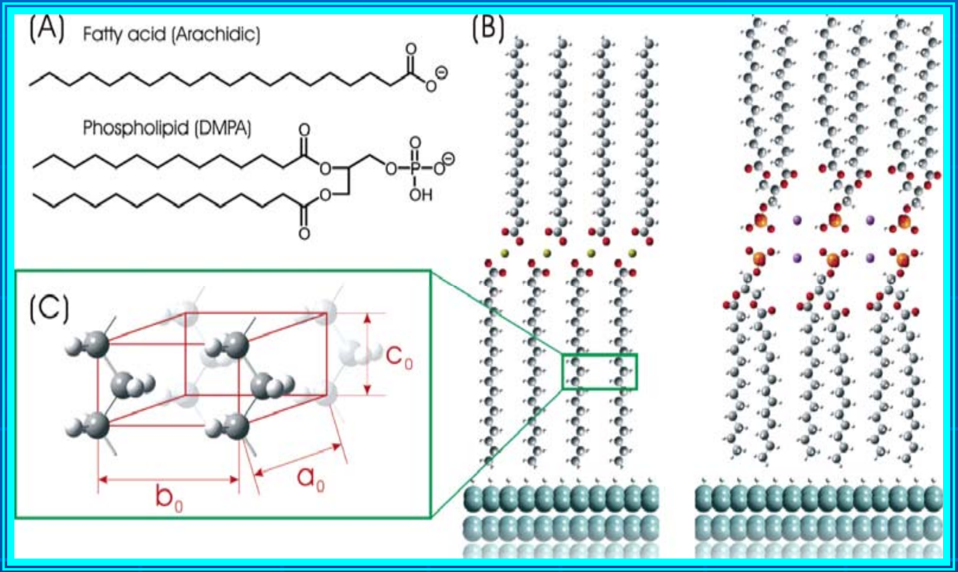
Dynamic

- Periodic expansion and contraction (thin film) or pure expansion (thick film)
- Non-local effect
- coherent (wave propagation)
- The magnitude of expansion is larger
- $\Delta s/s$ proportional to N (not saturated)
- $\Delta L/L \sim L^2$ (middle atoms expand more)

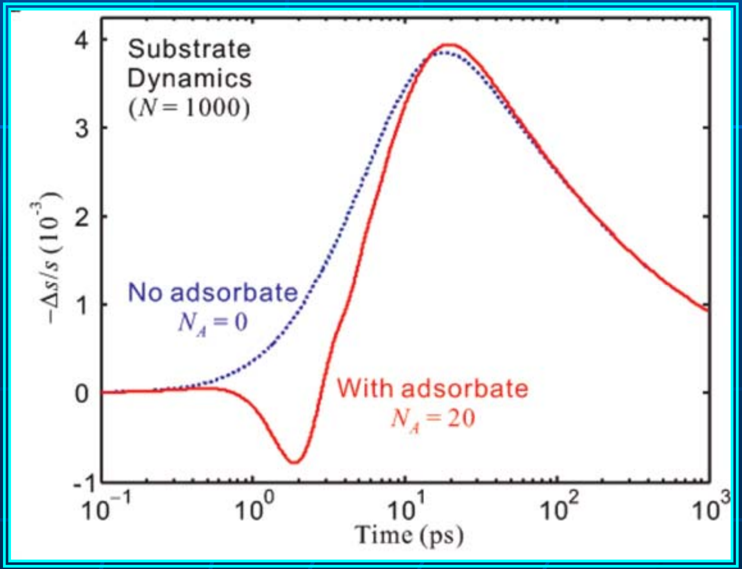
Static

- Only expansion occurs
- Local effect
- Non-coherent
- The magnitude of expansion is smaller
- $\Delta s/s$ independent of N
- $\Delta L/L \sim \Delta T$ independent of L

UEC of adsorbates & interfacial effects



Time dependence of
Bragg-spot shift



Laser-induced phase transition

in VO_2

Insulator ←→ Metallic

T_c ~ 340 K

Eg = 0.7 eV

V. A. Lobastov, J. Weissenrieder, J. Tang and A. H. Zewail, **Nano Lett**. (2007)

Phase transition in VO_2

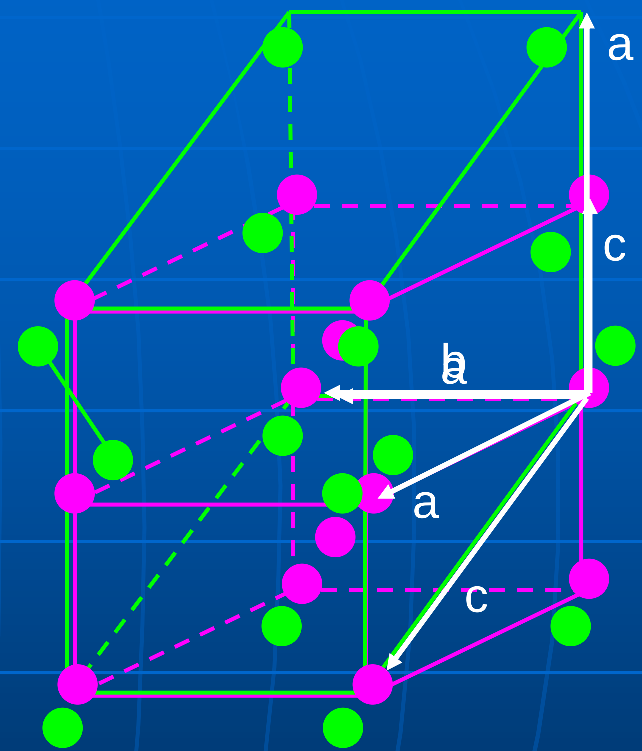
Insulator ↔ Metallic

Monoclinic Tetragonal (Rutile)

$a_m = 2c_r$

$b_m = a_r$

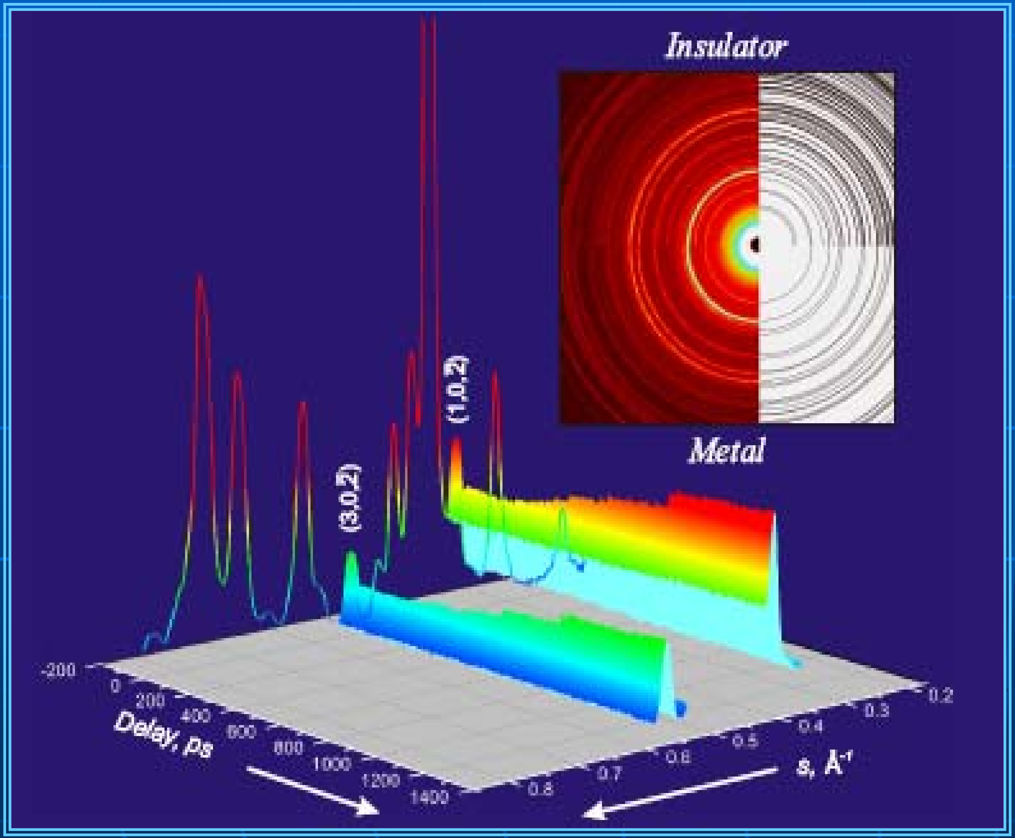
$C_m = a_r - c_r$



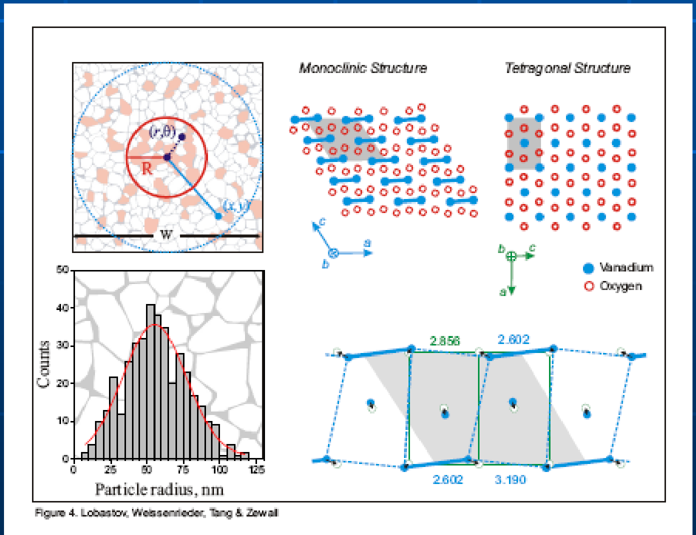
V-V bond

Electron diffraction pattern

Measured and simulated electron diffraction patterns

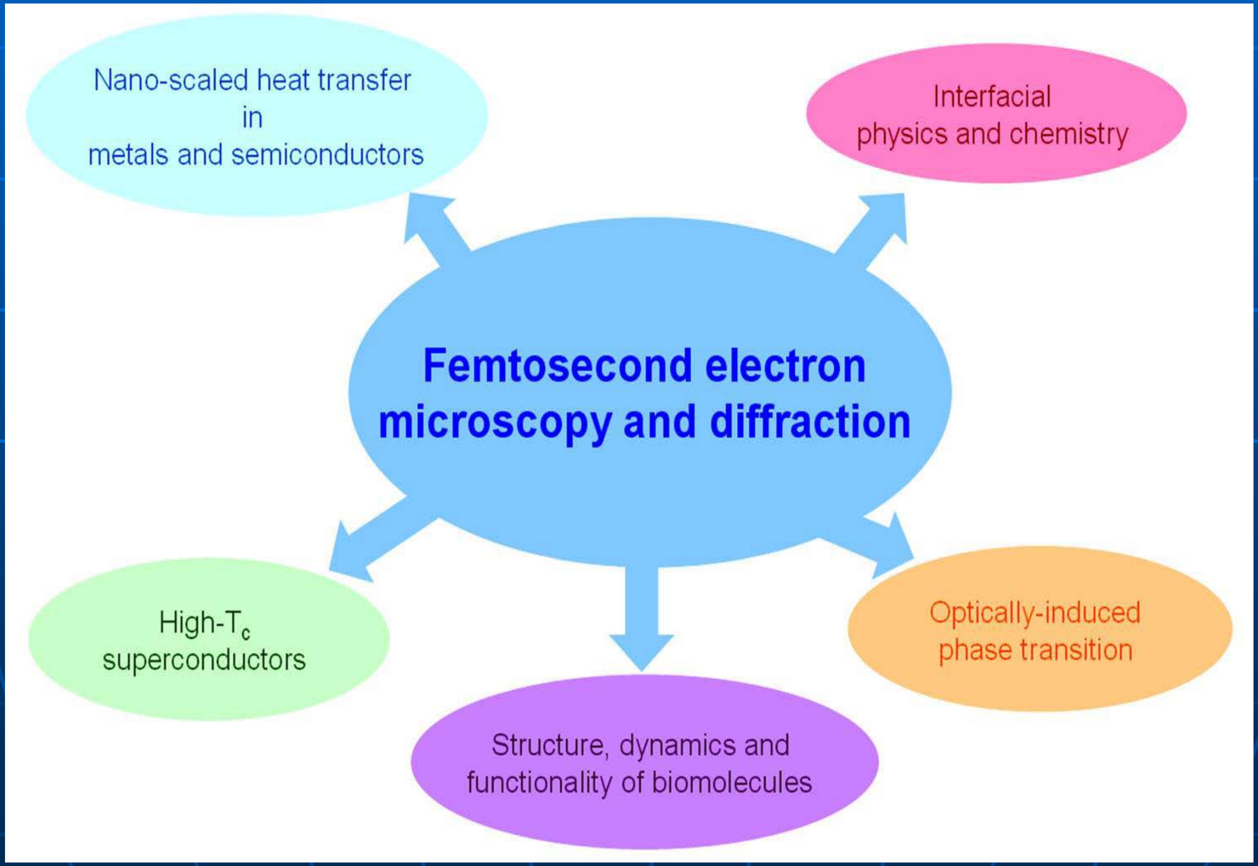


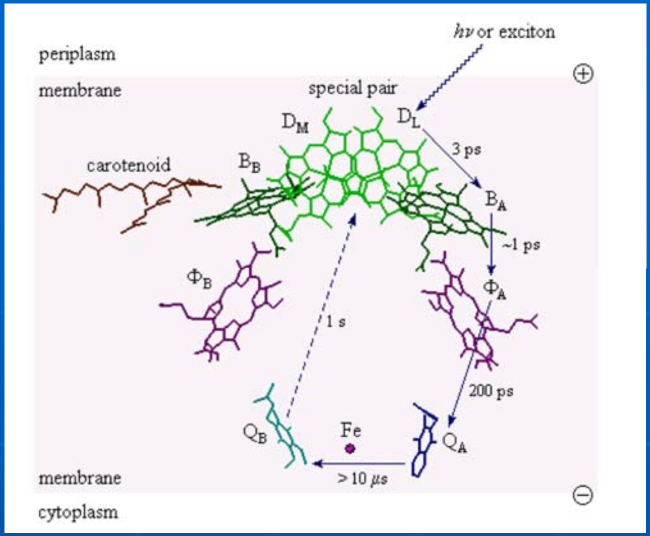
Electron gun: 120 keV
Laser : 776 nm
Fluence: 0.05 mJ/cm^2



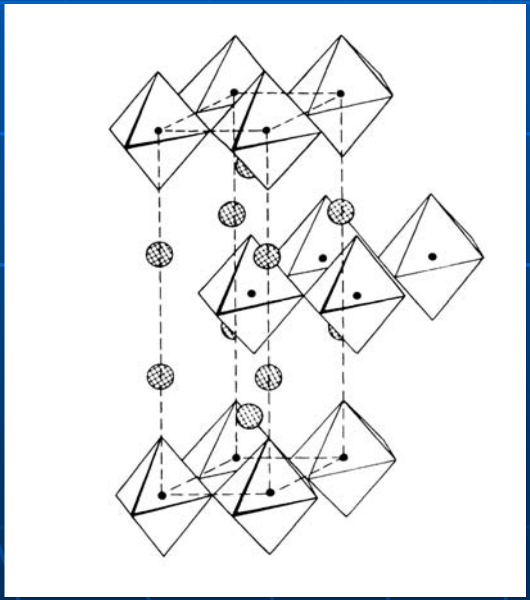
Natural Sciences: interfacial properties (surface physics, chemistry), nanoparticles, self-assembled monolayers, high Tc superconductors bond-breaking, conformation changes, etc.

Life Sciences: membrane protein, DNA, molecular recognition, hydration, charge transport, photosynthesis, etc.

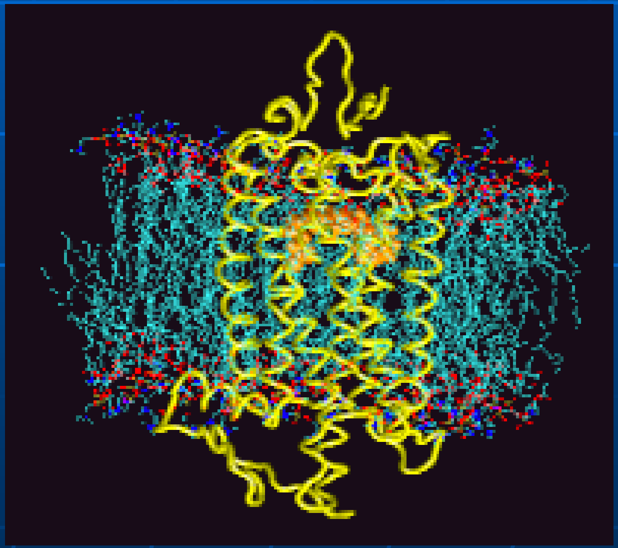




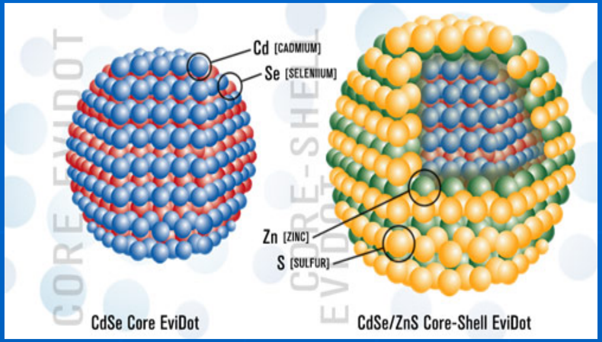
Photosynthetic RC



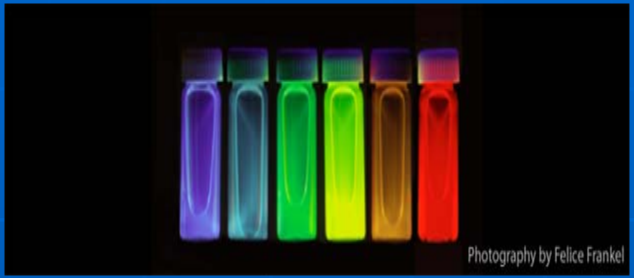
High Tc superconductor



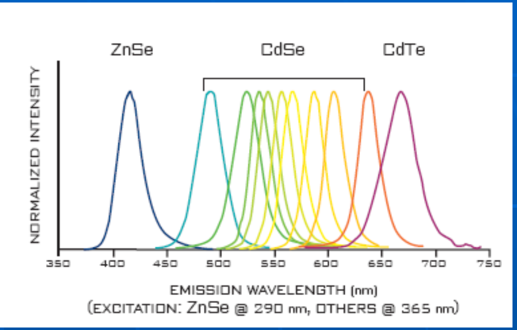
Rhodopsin



Quantum dots

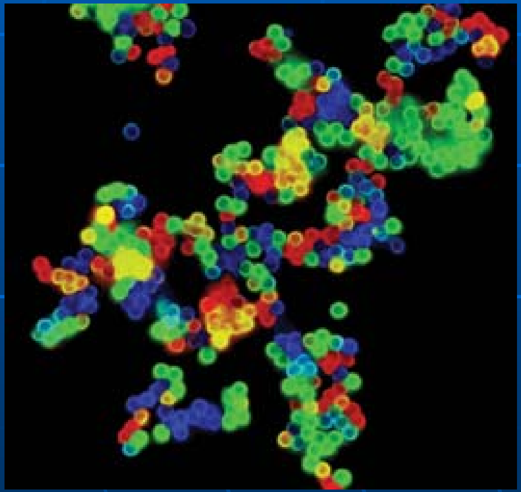


Emission spectra of QDs

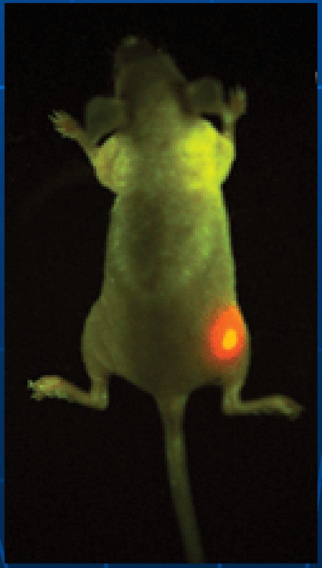


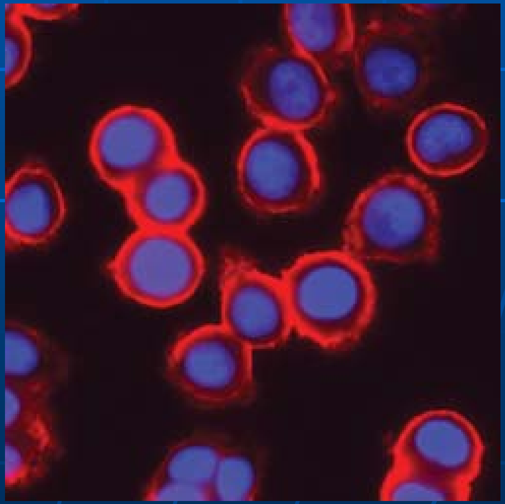
Polymer beads embedded with quantum dots fluoresce in five different colors.

labeling tags



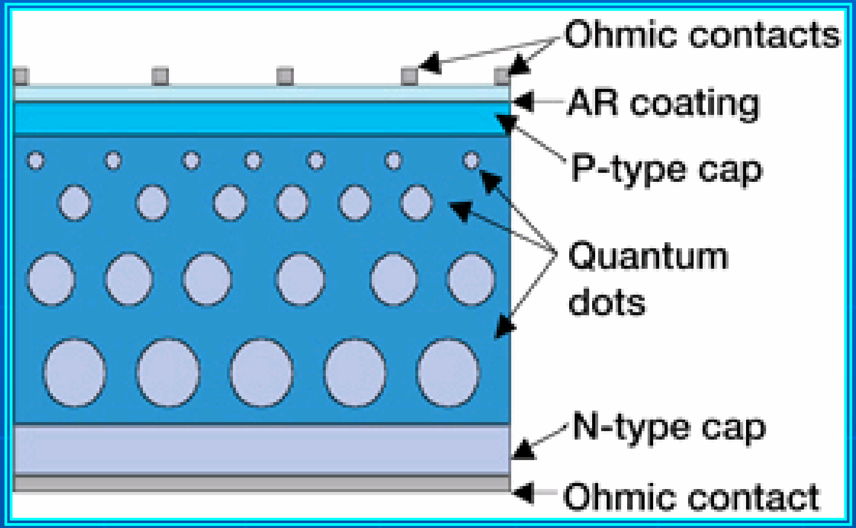
Red QDs injected into a live mouse mark the location of a tumor.
C. Seydel, *Science***, 2003**, 300, 5616.





Red light-emitting quantum dots tag proteins on the surfaces of breast cancer cells.

Potential applications

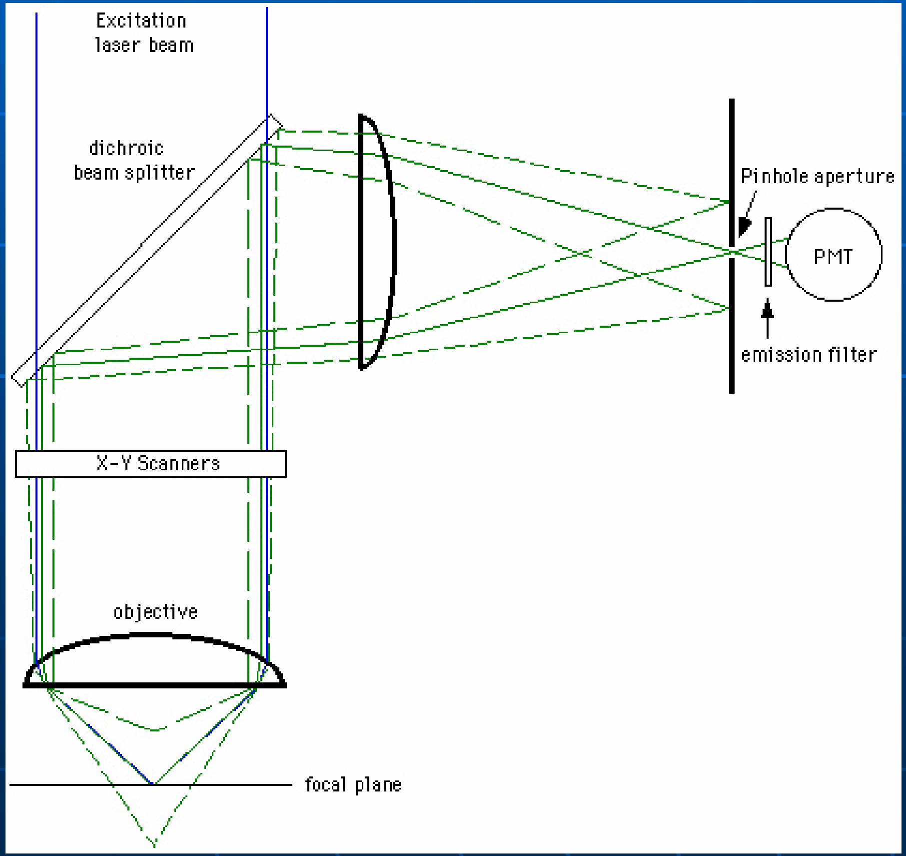


Intermediate-bandgap solar cell

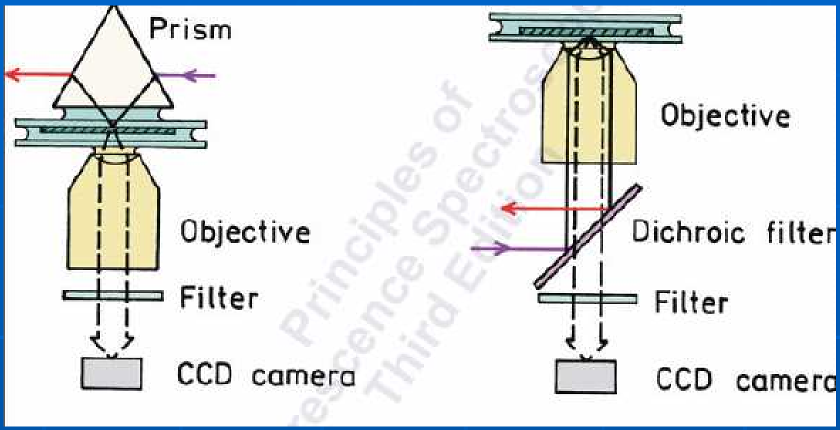
Labeling tags
Solar cells
White LEDs
(LED Wavelength Converter)
Military Applications (Infrared Paints)
InAs/GaAs-based quantum dot laser
High density memory
Quantum computing

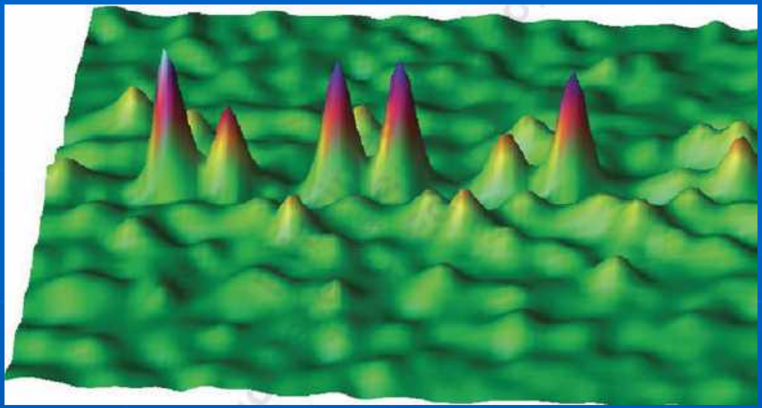
Confocal microscopy

The microscope is able to filter out the out-of-focus light from above and below the point of focus in the object. A "pinhole" situated in front of the image plane which acts as a spatial filter and allows only the in-focus portion of the light to be imaged

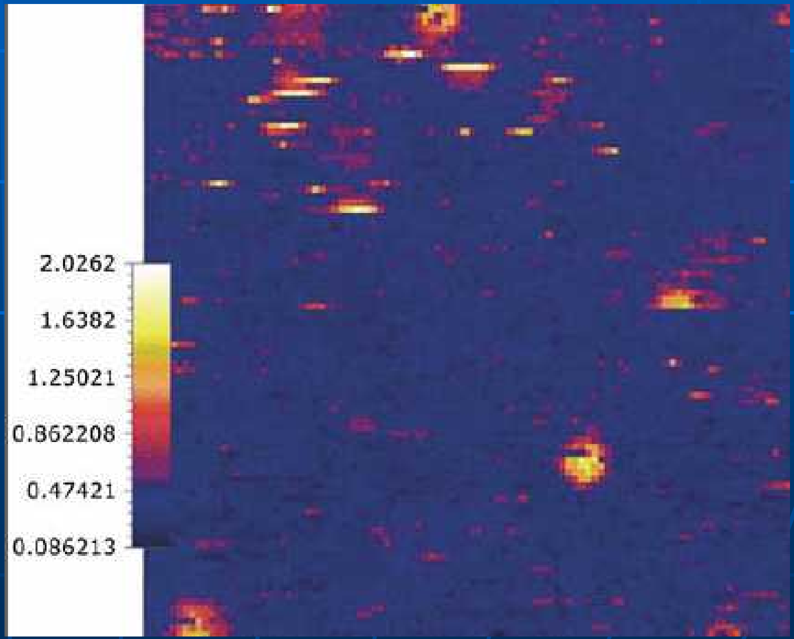


Inverted microscope





Green fluorescent protein



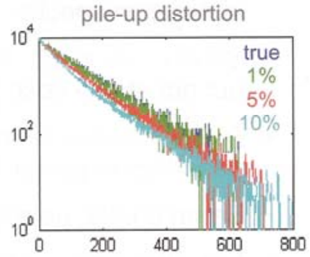
10 µm x 10 µm

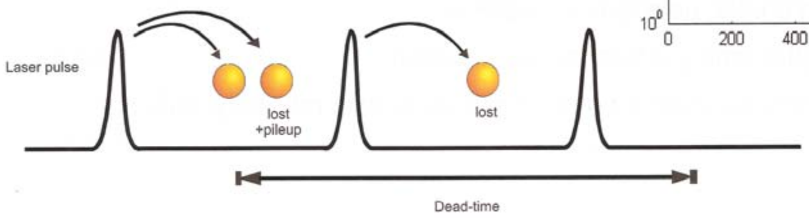
TCSPC Disadvantages and Difficulties

- Need pulsed light source and fast electronics (no problem today)
- Need fast single photon detector (can be difficult in the IR)
- Considered complicated & expensive (not true today)

Specific Difficulties:

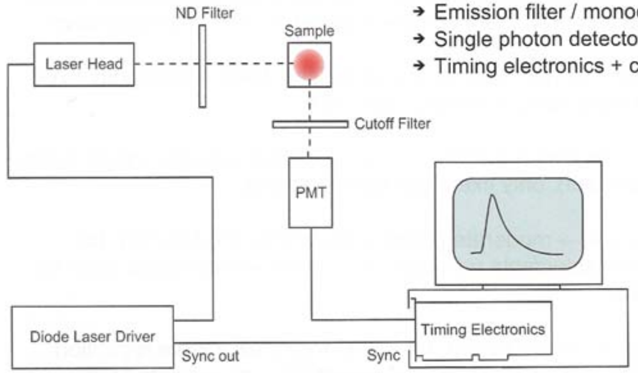
- Pile-up → keep count rate < 1..2%, use high laser pulse rate
- Dead-time → keep count rate < 1..2%, correct intensities





9

Basic TCSPC / TR-Fluorescence Setup

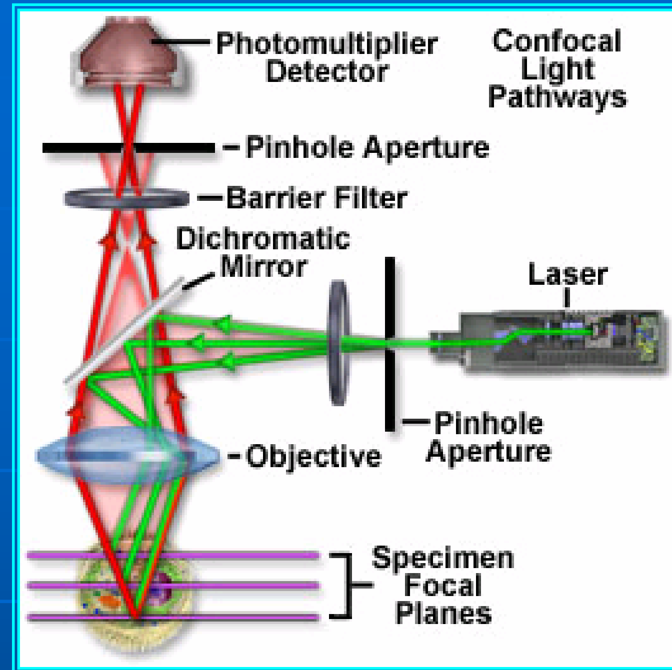


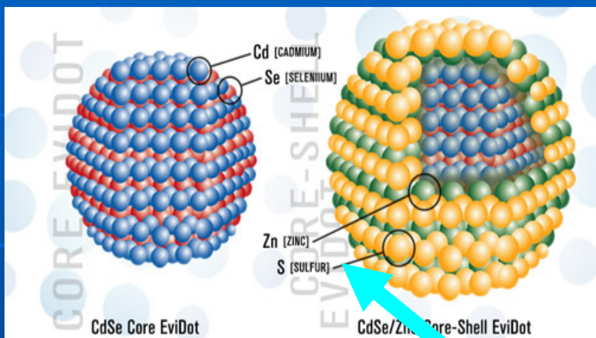
Typical system components:

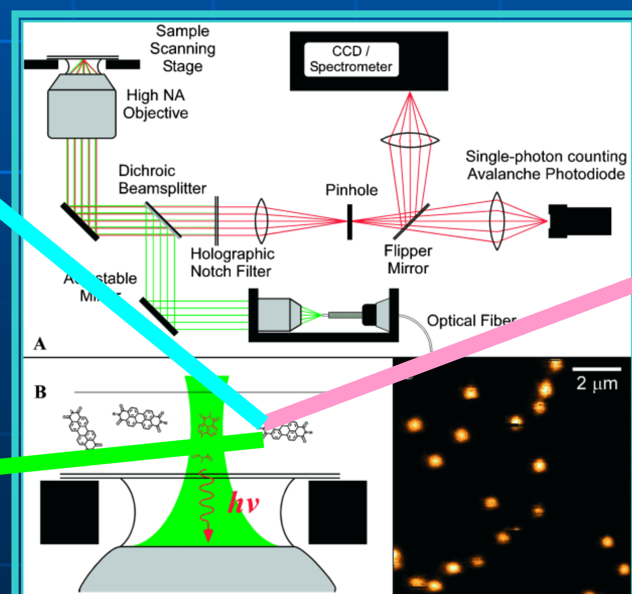
- → Pulsed excitation light source
- → Excitation filter / monochromator
- → Emission filter / monochromator
- → Single photon detector
- → Timing electronics + computer

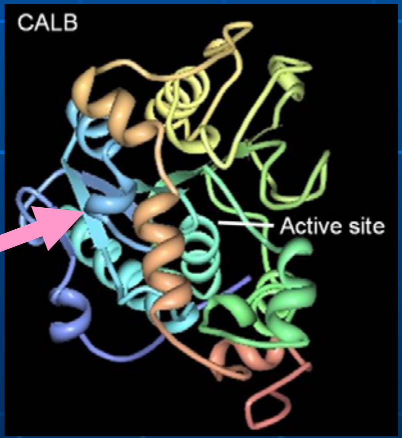
10

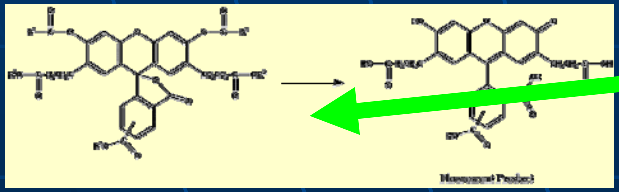
Confocal microscopy & Single-Particle Intermittency





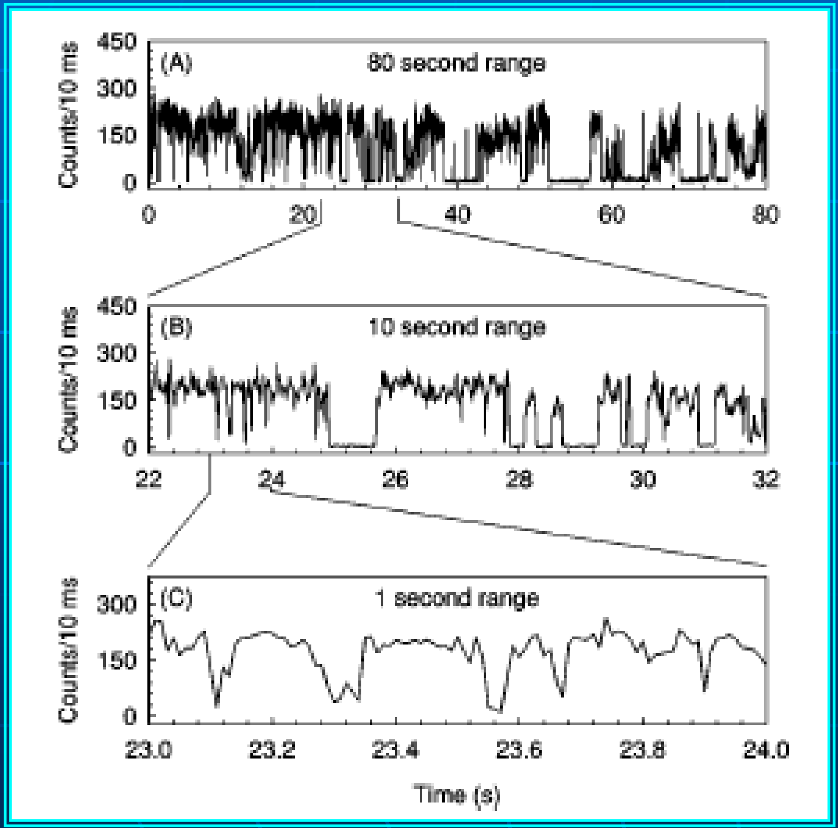




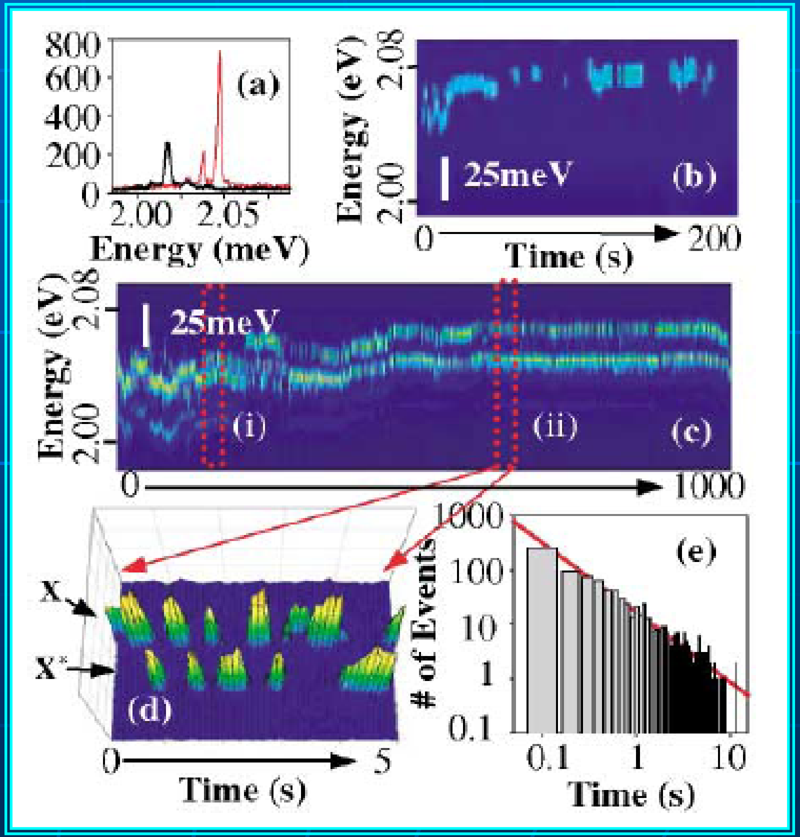


Fluorescence intermittency (blinking)

histogram

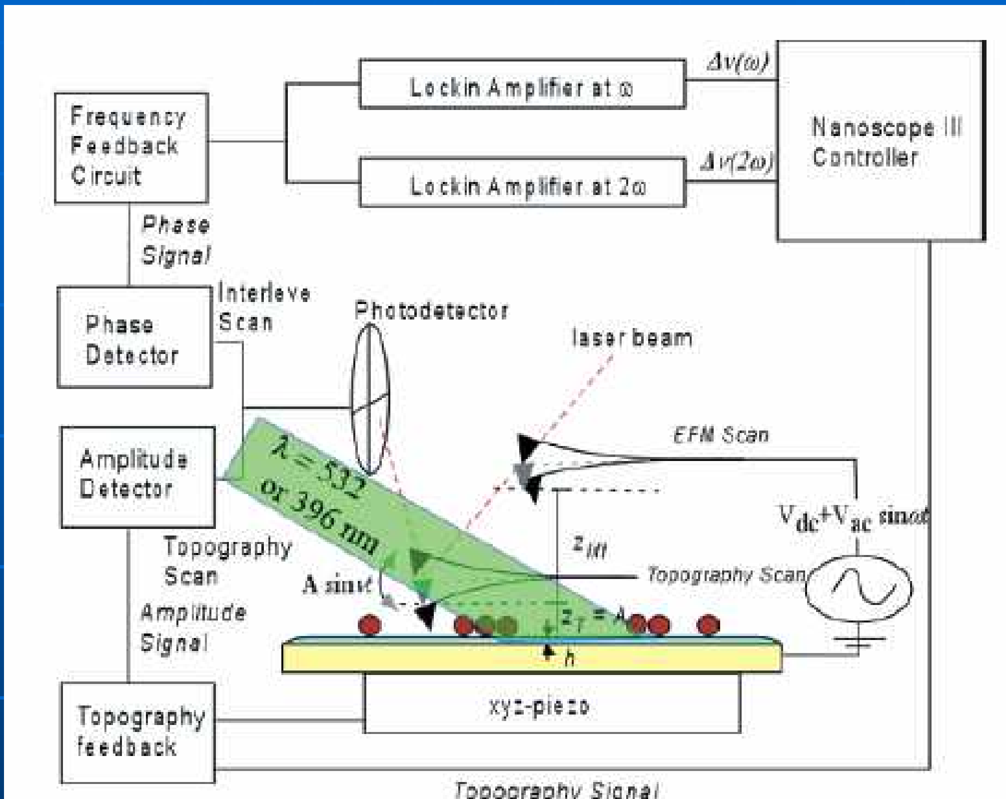


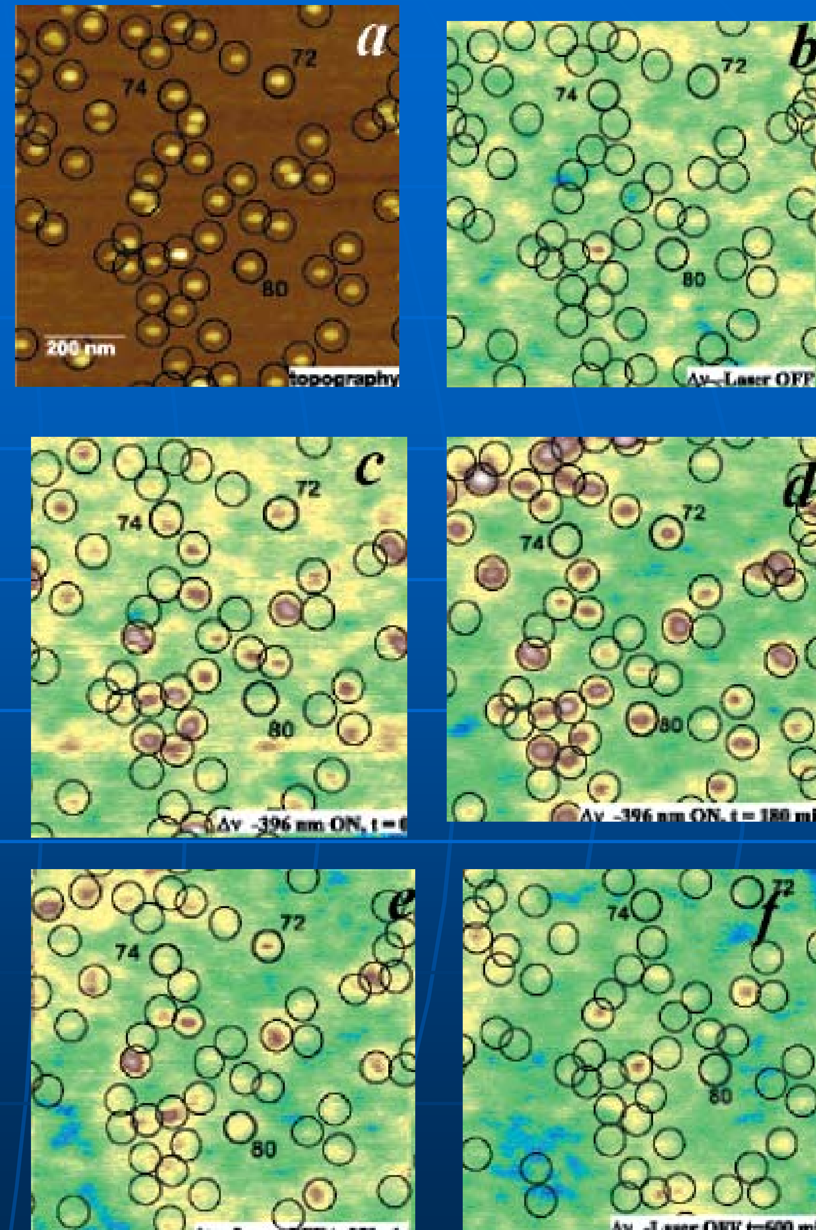
D. Nesbitt *et al*; *J. Chem. Phys.* **2000**



M. G. Bawendi., *et al. PRL* **2002**

Electrostatic force microscopy of CdSe





a) **Topography of CdSe QDs**

Charge map $10^3 \times 10^3$ nm^2

b) Before illumination
C-d) *light-on*
e) 4 hrs f) 10 hrs after light -off

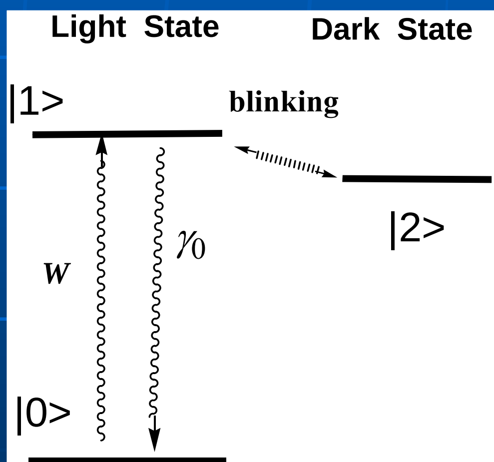
L. Brus, *et al. J. Phys. Chem. B*, **2004**, 108, 4946

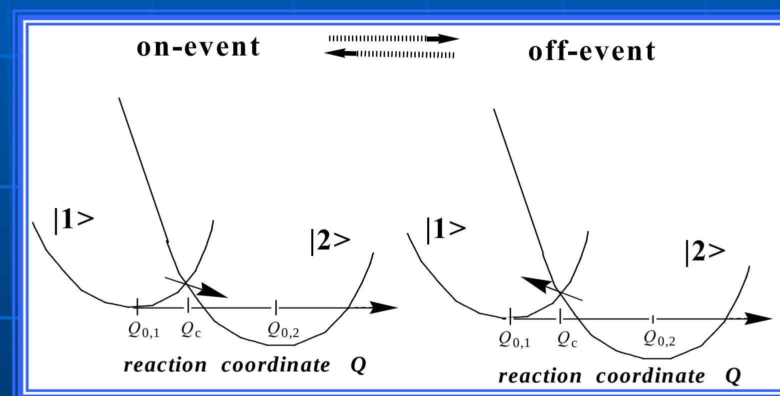
- **Why does a QD blink ?**
- **What causes a power law distribution (t^{-m}) ?**
- **Why is the exponent *m* close to 3 / 2 ?**

Diffusion-controlled electron transfer (DCET) model

(Tang & Marcus, PRL and JCP , 2005)

Neutral light state ←→ Positively charged dark state





1-D diffusion in energy space

$$\frac{\partial}{\partial t}\rho_1(Q,t) = L_1\,\rho_1(Q,t) - C_1\,\rho_1(Q,t)$$

$$\frac{\partial}{\partial t}\rho_2(Q,t) = L_2\,\rho_2(Q,t) - C_2\,\rho_2(Q,t)$$

$$L_k = D_k(t)\frac{\partial}{\partial Q}\left(\frac{\partial}{\partial Q} + \frac{1}{k_B T}\frac{\partial}{\partial Q}U_k(Q)\right)$$

$$C_k = \frac{2\pi\,|V_k|^2}{\hbar}\delta\big(U_{12}(Q)\big)$$

DCET model for power-law intermittency

Blinking statistics ***P(t):*** waiting time distribution for "on" or "off" events

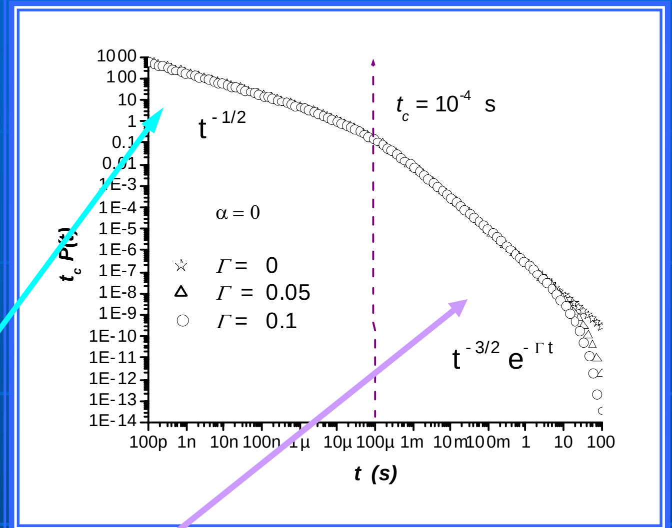
$$\overline{P_k}(s) = -\int_0^\infty dt\, e^{-st} \frac{d}{dt}\left(\int_{-\infty}^{\infty} dQ\, \rho_k(Q,t)\right) = \frac{A_k \overline{G}_k(Q_c,Q_c;s)}{1 + A_k \overline{G}_k(Q_c,Q_c;s)}$$

$$A_k = \frac{2\pi}{\hbar} |V_k|^2 \left|\partial\left(U_1(Q) - U_2(Q)\right)/\partial Q\right|_{Q=Q_c}$$

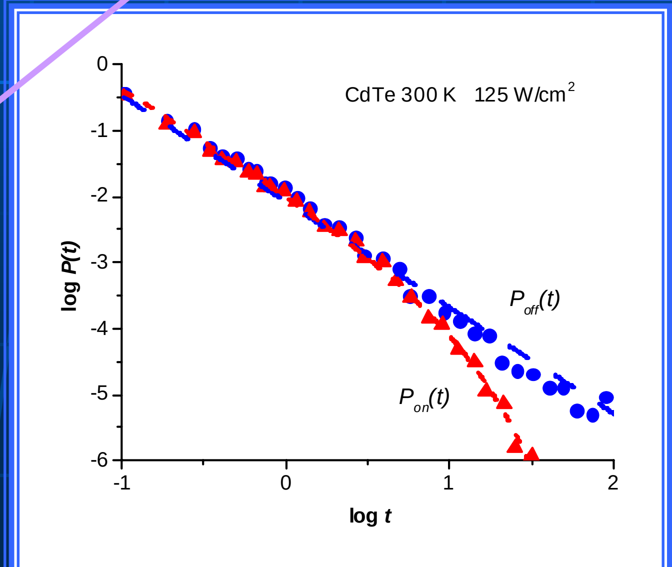
Debye medium (D is a constant)

$$P_k(t) \sim \frac{1}{\sqrt{\pi t_{c,k}}} t^{-1/2} \qquad \text{if } t \ll t_{c,k}$$

$$P_k(t) \sim \frac{\sqrt{t_{c,k}}}{2\sqrt{\pi}} t^{-3/2} \exp(-\Gamma_k t) \qquad \text{if } t_{c,k} \ll t \ll \tau_{L,k}$$



CdTe

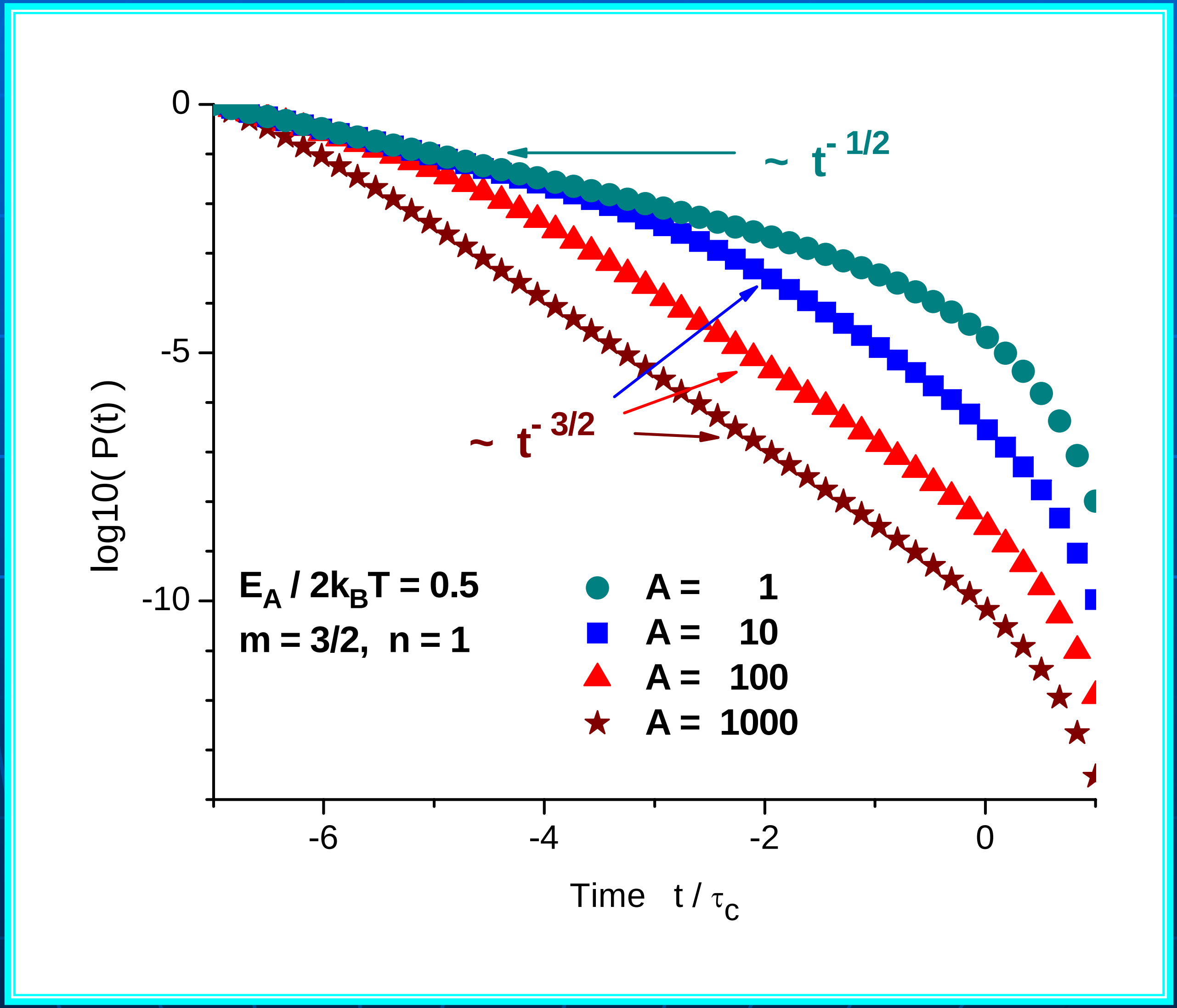


$$P_k(t) = \frac{1}{\sqrt{\pi t_{c,k} t}} \left[1 - \sqrt{\pi t / t_{c,k}} \exp(t/t_{c,k}) \; erfc\left(\sqrt{t/t_{c,k}}\right)\right] \exp(-\Gamma_k t),$$

(DCET model)

Small A:
weak coupling

Large A:
strong coupling



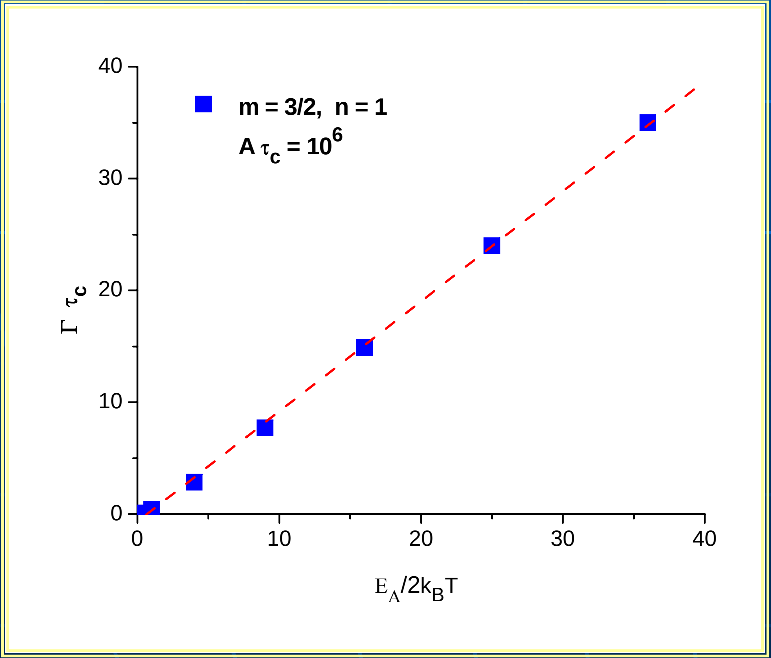
Bending rate Γ at longer times

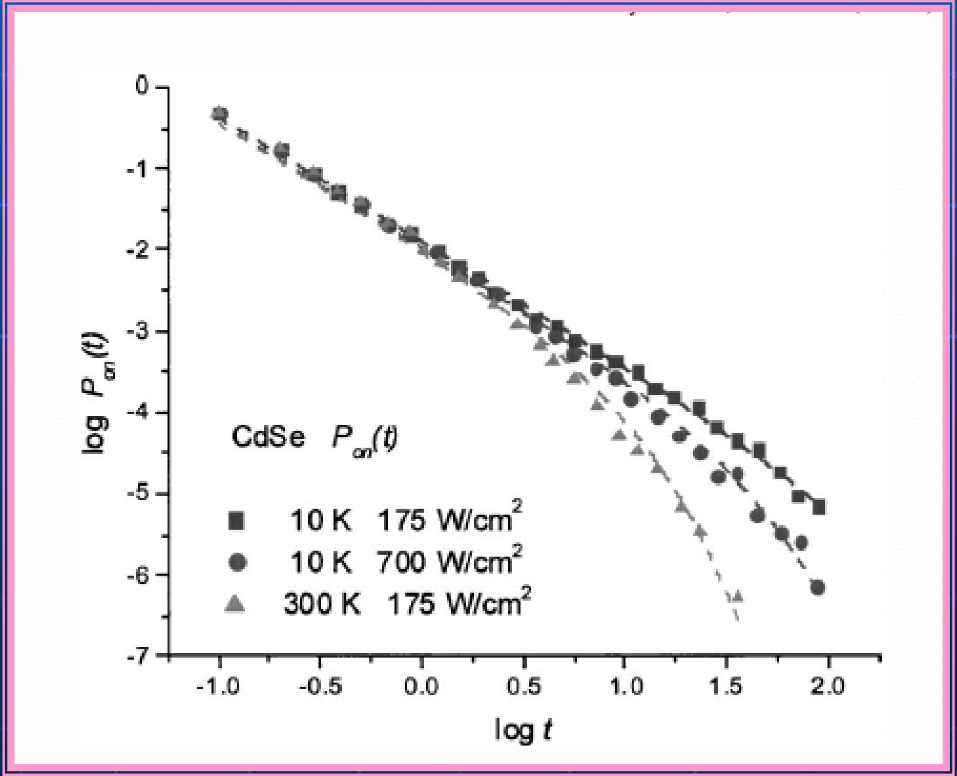
DCET model

$$\Gamma_k \tau_k \equiv \frac{E_{A,k}}{2k_B T},$$

$$E_{A,1} \equiv \frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda}, \quad E_{A,2} \equiv \frac{\left(\lambda - \Delta G^0\right)^2}{4\lambda}$$

Bending rate and diffusion rate increase with:
Light intensity and QD size
Temperature (faster diffusion)





Normal *vs.* anomalous diffusion

$$L_k = D_k(t)\frac{\partial}{\partial Q}\left(\frac{\partial}{\partial Q} + \frac{1}{k_B T}\frac{\partial}{\partial Q}U_k(Q)\right)$$

Debye dielectric medium

$$\bar{\chi}(s) = 1/(1+s\,\tau_D) \qquad \bar{\tau}_{L,k}(s) = \tau_{L,k} \equiv \tau_{D,k}\varepsilon_\infty/\varepsilon_0\,,$$

$$\Theta_k(t) = \exp(-t/\tau_{L,k}) \qquad D_k(t) = \Delta_k^2/\tau_{L,k}$$

$$\sigma^2(t) = <(Q(t) - <Q(t)>)^2> \approx 2(\Delta^2\tau_D/\tau_L)t$$

$$D_k(t) = -\Delta_k^2\,\frac{d}{dt}\ln\Theta_k(t)\,,\quad \Theta_k(t) \equiv L^{-1}\left(\frac{1}{s + \frac{1}{\bar{\tau}_{L,k}(s)}}\right)$$

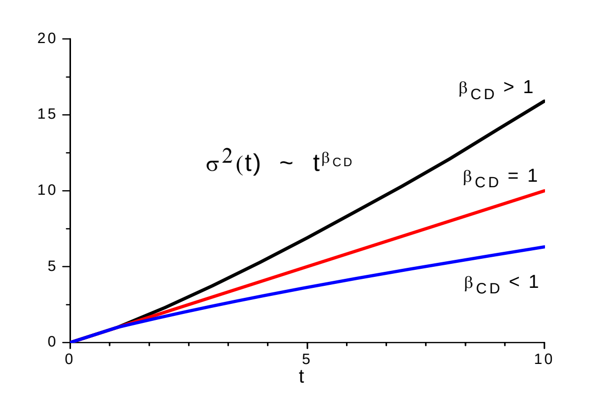
$$\bar{\tau}_{L,k}(s) = \frac{\varepsilon_\infty}{\varepsilon_0}\,\frac{1-\bar{\chi}_k(s)}{s\,\bar{\chi}_k(s)}\,,\qquad \bar{\chi}_k(s) = \frac{\bar{\varepsilon}_k(s) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}.$$

$$\sigma^2(t) \sim t^{\beta_{CD}}$$

$\beta_{CD} < 1$ (subdiffusion)

$\beta_{CD} = 1$ (normal diffusion)

$\beta_{CD} > 1$ (superdiffusion)



Cole-Davison medium

$$\bar{\chi}(s) = 1/(1+s\,\tau_D)^{\beta_{CD}}$$

D(t) is time-dependent

More general anomalous diffusion

J. Tang, PR B (2007)

$$\frac{\partial}{\partial t} G(Q, Q'; t) = \frac{\partial}{\partial Q}\left(D_2(t) \frac{\partial}{\partial Q} + D_1(t)\ Q \right) G(Q, Q'; t) .$$

$$D_1(t) = -\frac{d}{dt} \ln \langle Q(t) \rangle$$

$$G(Q, Q'; t) = \frac{1}{\sqrt{2\pi \Delta_2(t)}} \exp\left[-\frac{(Q - Q' \Delta_1(t))^2}{2\Delta_2(t)} \right]$$

$$D_2(t) = D_1(t)\ \Delta_2(t) + \frac{1}{2} \frac{d}{dt} \Delta_2(t) .$$

$$\Delta_1(t) \approx 1 - (t/\tau_c)^{\nu}$$

Kohlrausch-Williams-Watts mode
(Havriliak-Negami dielectric function)

$$\Delta_2(t) \approx \Delta_2(\infty) \left(t/\tau_c \right)^{\mu}$$

$$\varepsilon(\omega) = \varepsilon_\infty + \Delta\varepsilon \Big/ \left[1 + (i\,\omega\,\tau_{HN})^{\alpha} \right]^{\gamma}$$

Ornstein-Uhlenbeck process: $\mu = \nu = 1$; D_1, D_2: constant

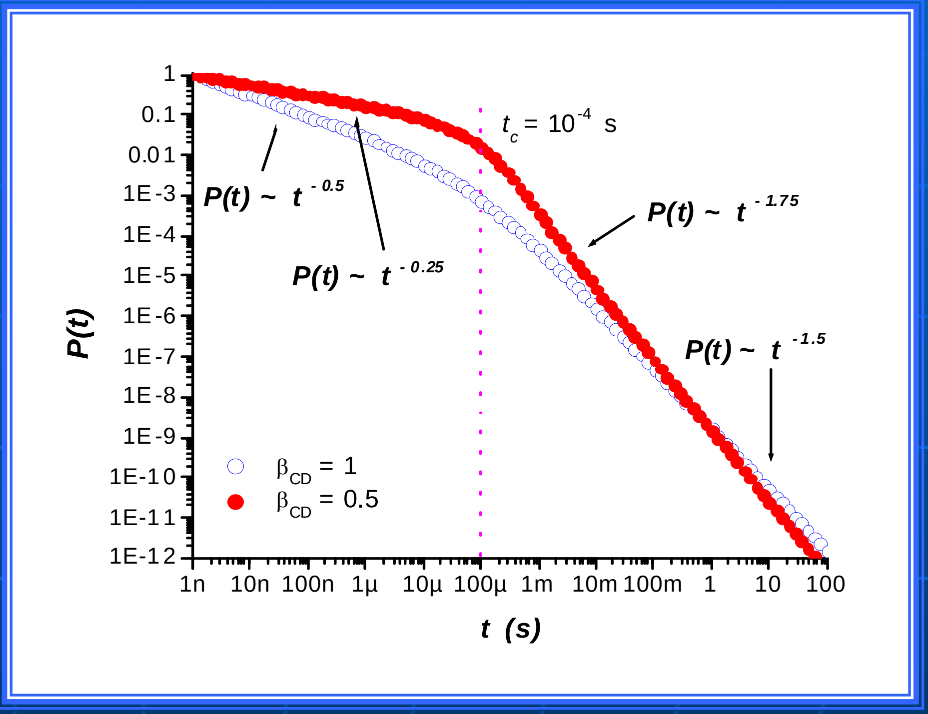
Non-Debye medium (anomalous diffusion)

J. Tang and R. A. Marcus, PRL and JCP (2005)

$$\bar{P}_k(s) \approx \frac{1}{1+\left(\left(s+\Gamma_k\right)t_{c,k}\right)^{1-\beta_{CD}/2}}$$

Mittag-Leffler function

$$E_a(z)=\sum_{n=0}^{\infty} z^n/\Gamma(na+1).$$



$$P_k(t) \sim \frac{d}{dt}\left[E_{-1+\beta_{CD}/2}\left(-(t/t_{c,k})^{-1+\beta_{CD}/2}\right)\right]\exp(-\Gamma_k t) \quad \text{if} \quad t \le 1/\Gamma_k < \tau_{L,k}$$

$$P_k(t) \sim \left(t/t_{c,k}\right)^{-\beta_{CD}/2}/\Gamma\left(1-\beta_{CD}/2\right)t_{c,k}, \quad \text{if } t < t_{c,k}$$

$$P_k(t) \sim \left(t/t_{c,k}\right)^{-2+\beta_{CD}/2}\exp(-\Gamma_k t)/\left|\Gamma\left(\beta_{CD}/2-1\right)\right|t_{c,k} \quad \text{if} \quad t_{c,k} < t \le 1/\Gamma_k < \tau_{L,k}.$$

Blinking statistics of nanorods and size dependence

J. Tang, JPC (2007)

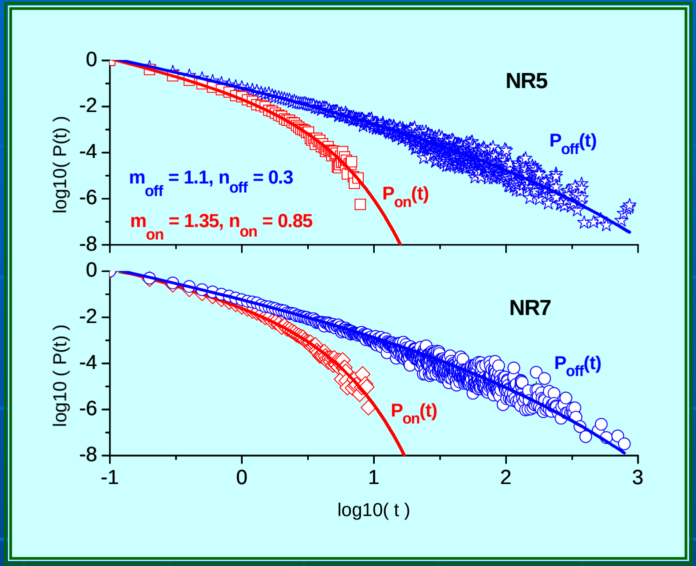
$$P(t) \approx P_0 \left(t/\tau_c\right)^{-2+\mu/2} \exp\left(-\left(\Gamma t\right)^{2\nu-\mu}\right)$$

$$\propto \quad t^{-m} \exp\left(-\left(\Gamma t\right)^{n}\right),$$

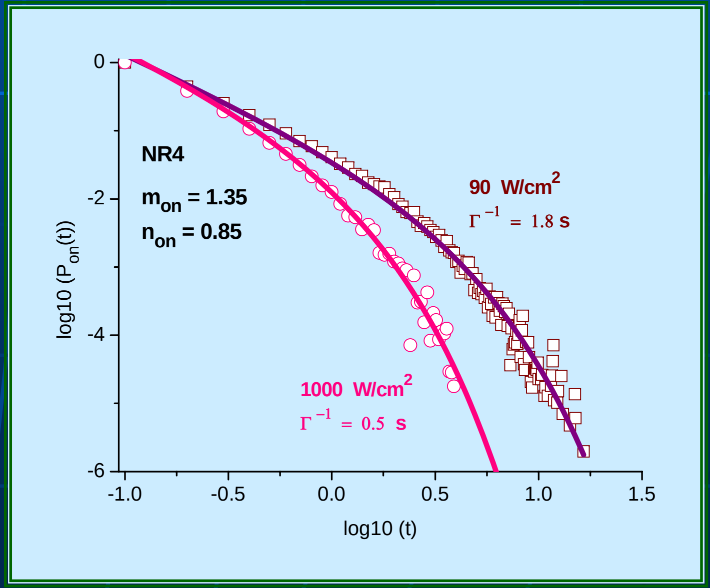
$m = 2 - \mu / 2$

$n = 2\nu - \mu$

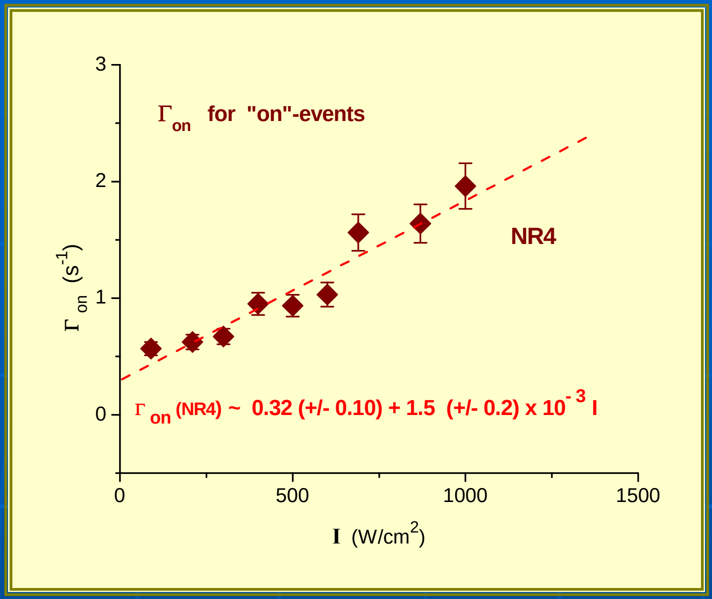
Size dependence



Intensity dependence

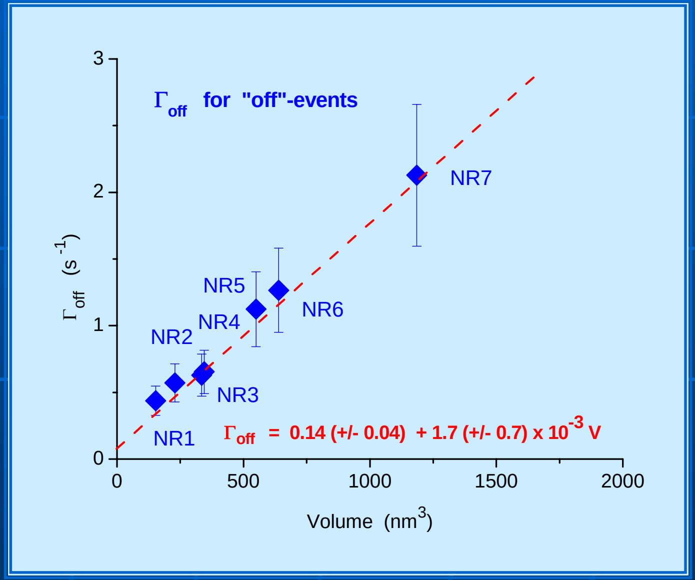


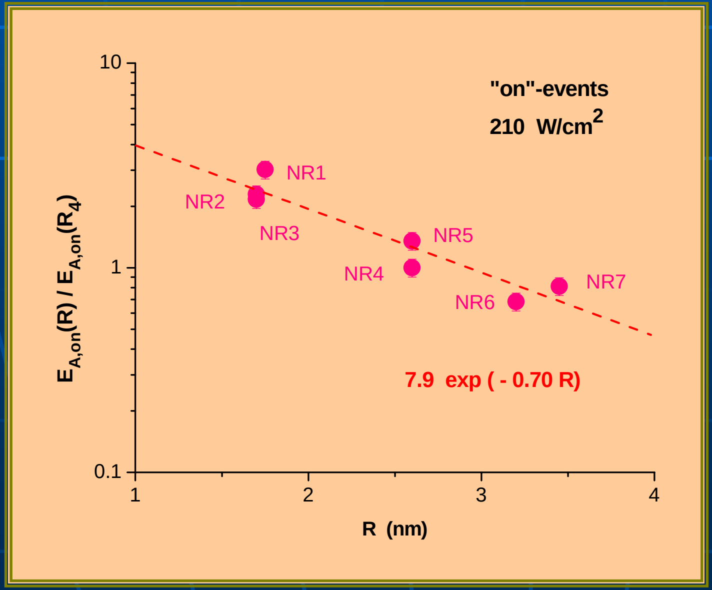
Light NRs



Intensity dependence

Dark NRs

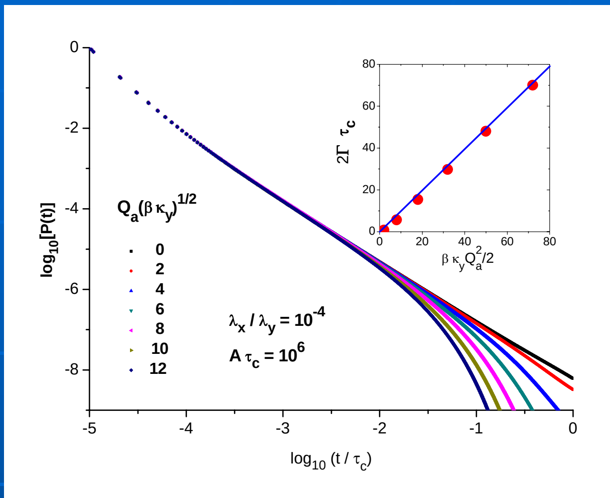




Volume dependence

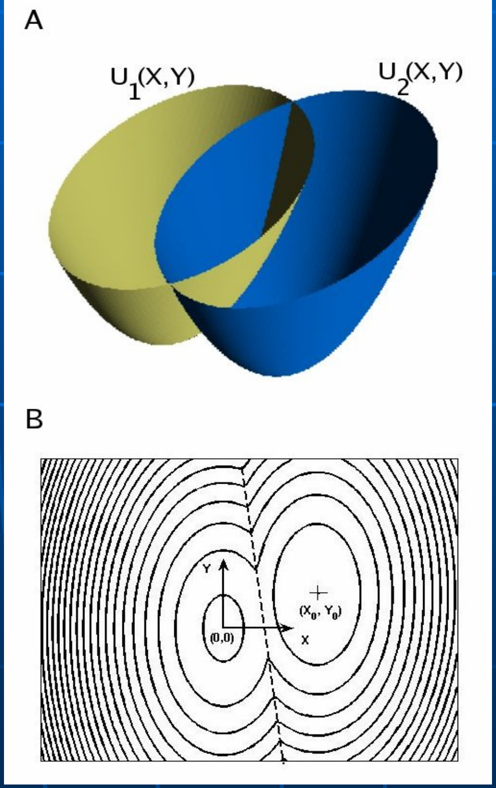
Radius dependence

Exotic power law for Si blinking



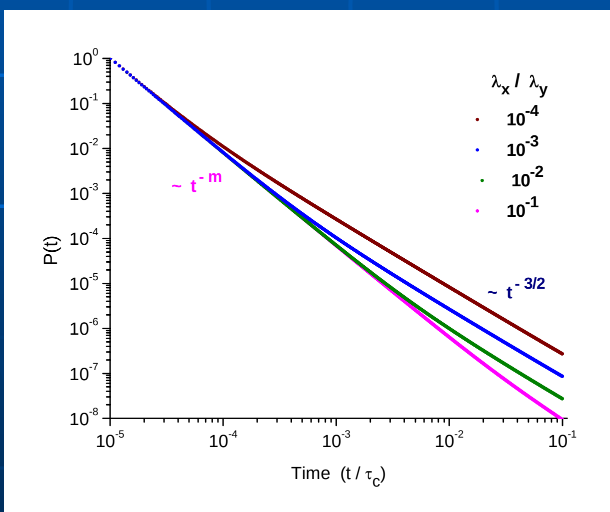
J. Tang, JCP (2007)

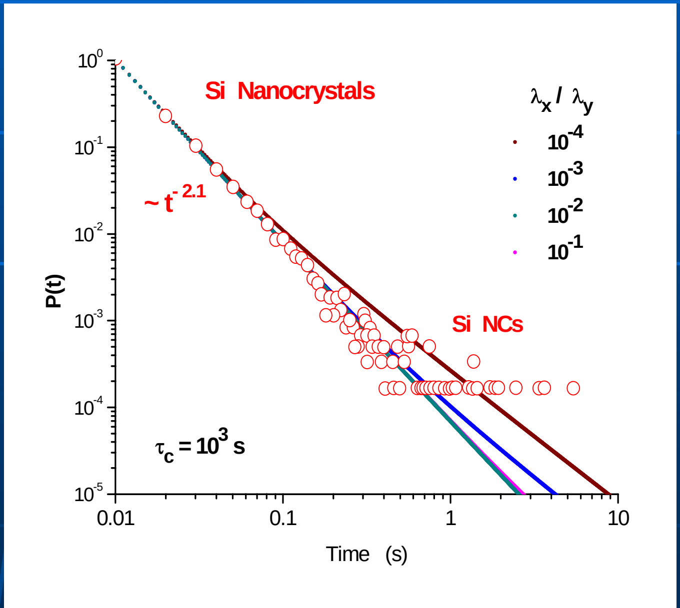
2-D model
Fast and slow
reaction coordinates



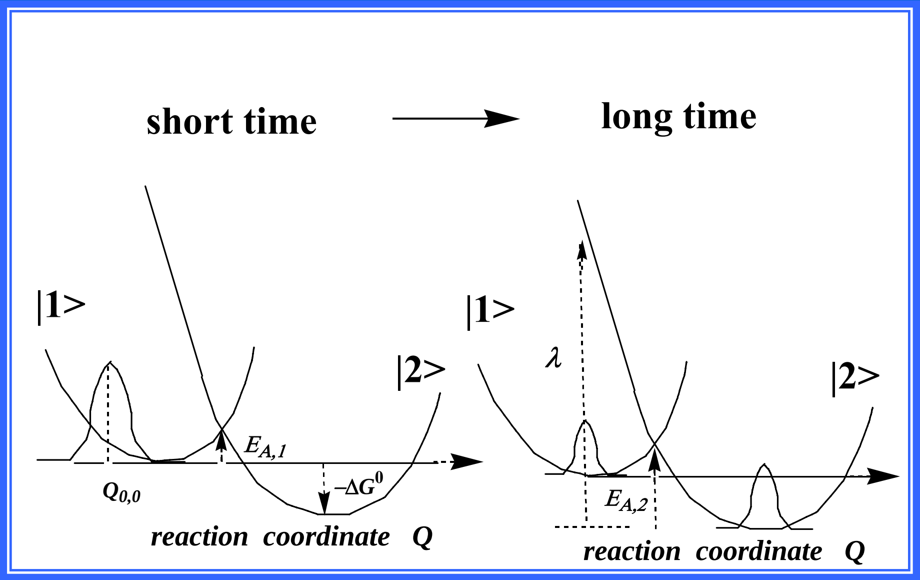
Crossing point is not like A δ-function

Power-law exponent Could be greater than 2



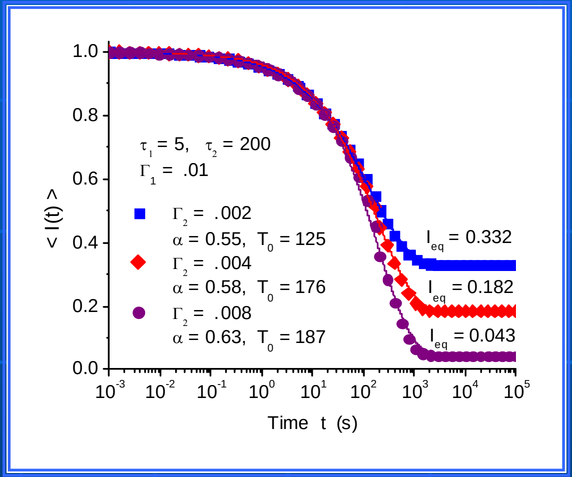


Ensemble fluorescence intensity decay



stretched exponential decay

$$I_{eq} + (1 - I_{eq})\exp\left(-\left(t/T_0\right)^{\alpha}\right)$$

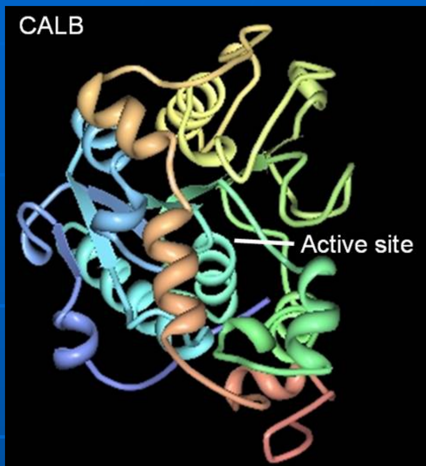


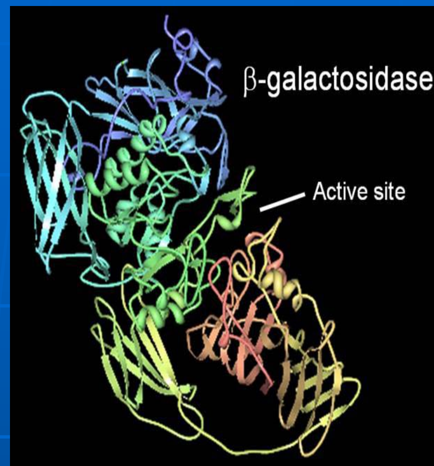
Single particle ***vs.*** **ensemble**

- Power-law decay
- distinguishable
- at the crossing initially
- nonergodic

- Stretched exponential decay
- indistinguishable
- in the ground state initially
- ergodic

Intermittency of single-enzyme activity

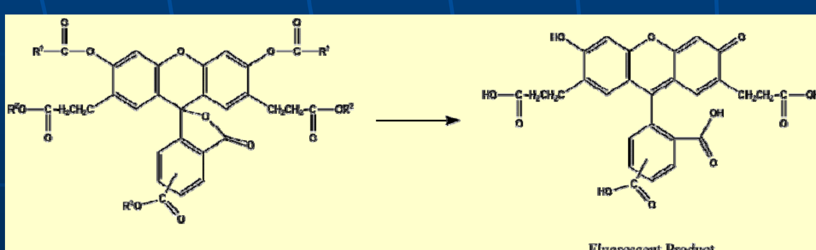




X. S. Xie, et al. Nature Chem. Bio. 2, 87 (2005)

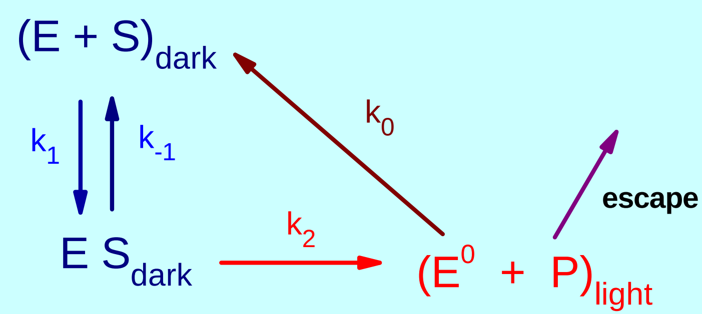
O. Flomenbom, et al., PNAS 102, 2368 (2005)

J. Tang, JPC (submitted)

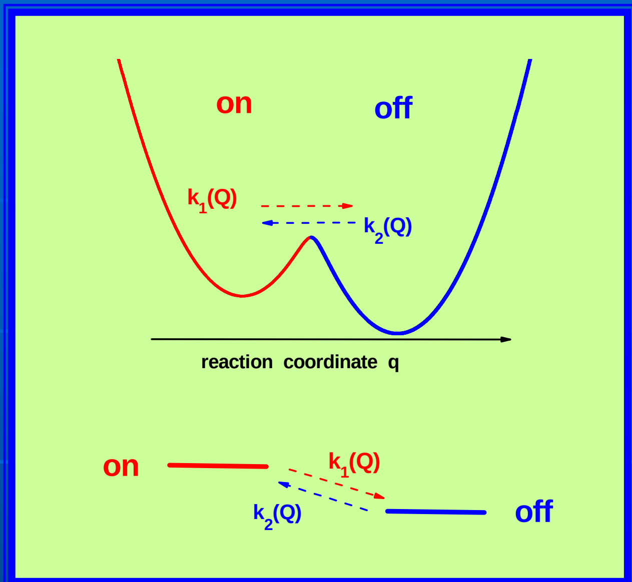


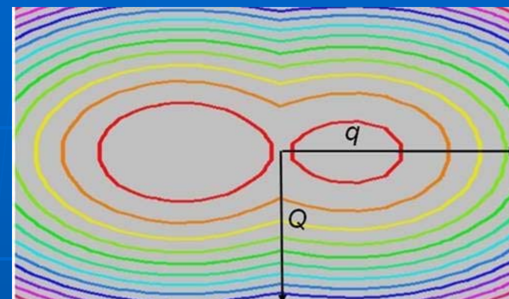
Michaelis-Menten Scheme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E\,S \xrightarrow{k_2} E^0 + P \qquad E^0 \xrightarrow{k_0} E$$



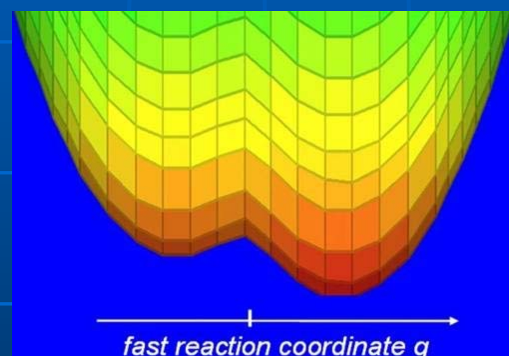
Michaelis-Menten scheme for enzyme reactions

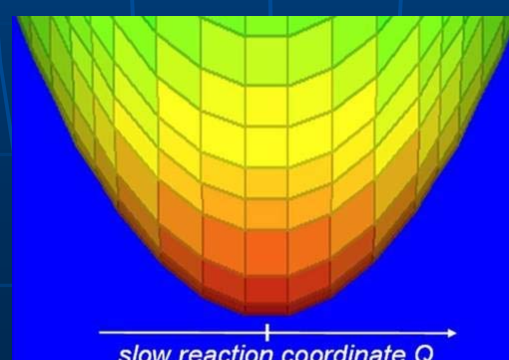


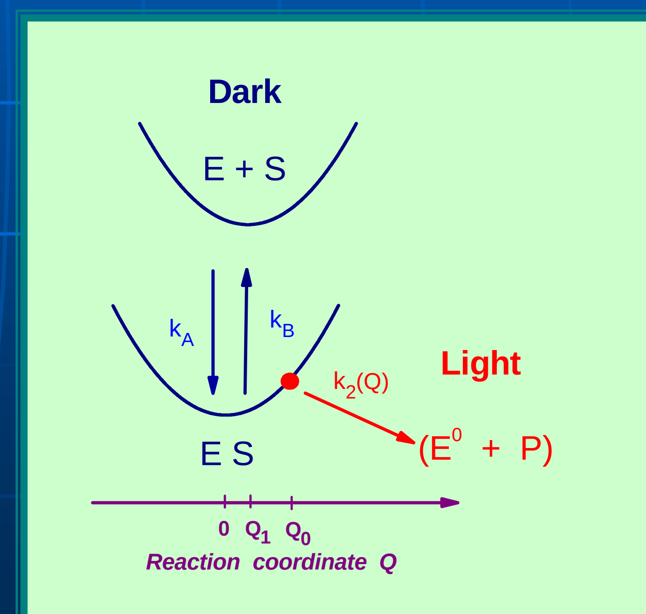


$$P(t) = \frac{k_A k_2}{\lambda_2 - \lambda_1}\left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$

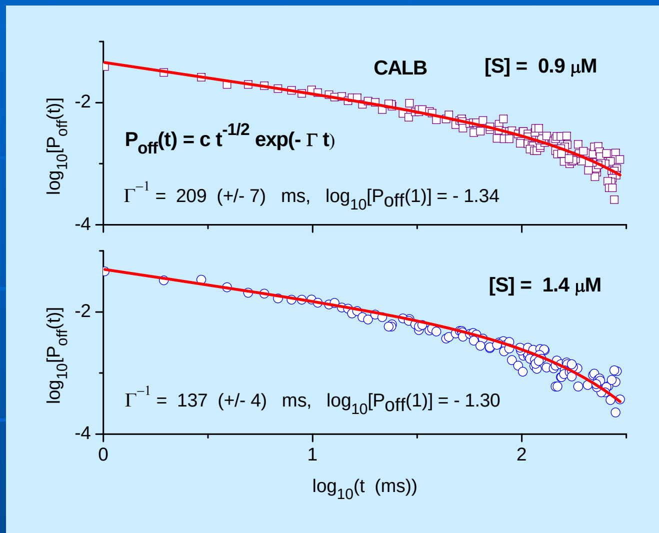
$$\lambda_{1,2} = k_A + k_B + k_2 \mp \sqrt{(k_A + k_B + k_2)^2 / 4 - k_A k_B}\,.$$

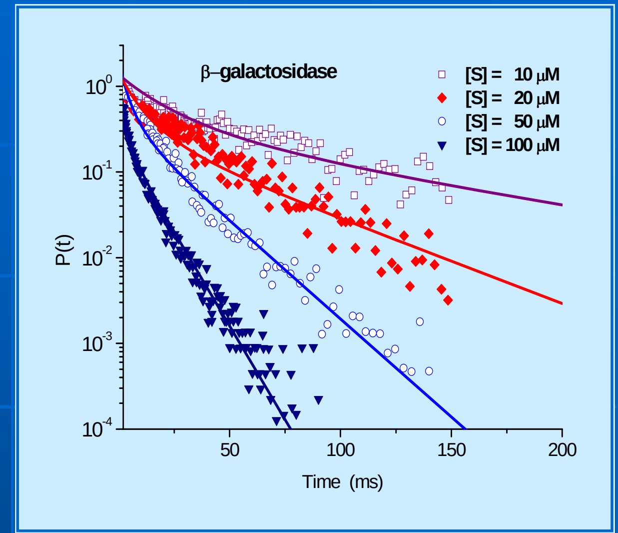


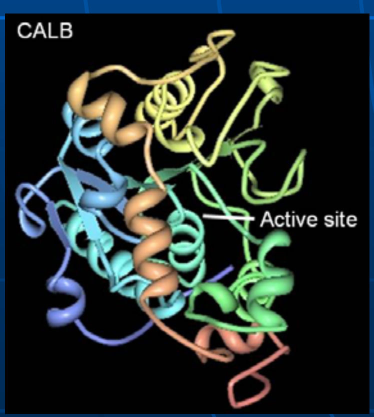


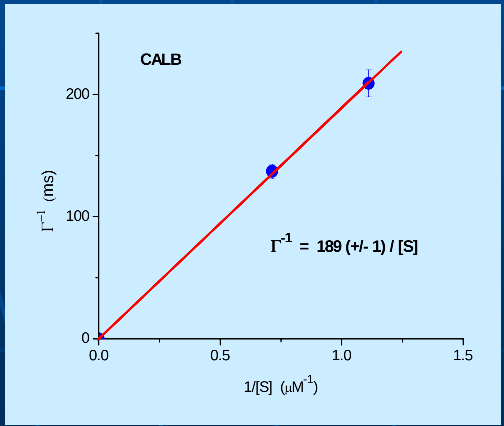


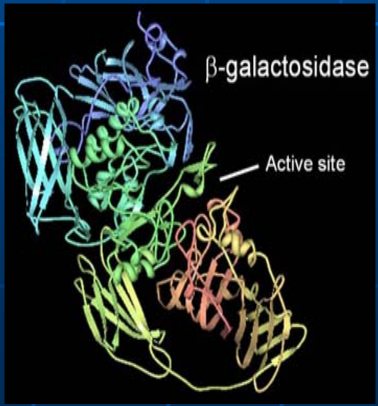
Diffusion-controlled Michael-Menten reaction

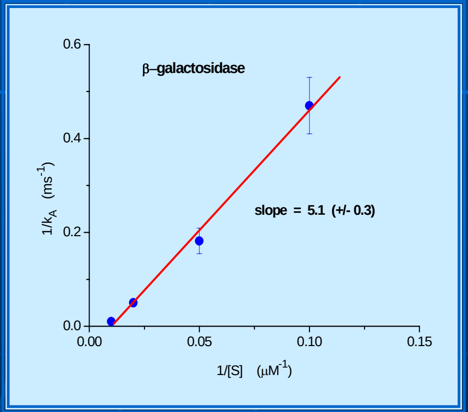










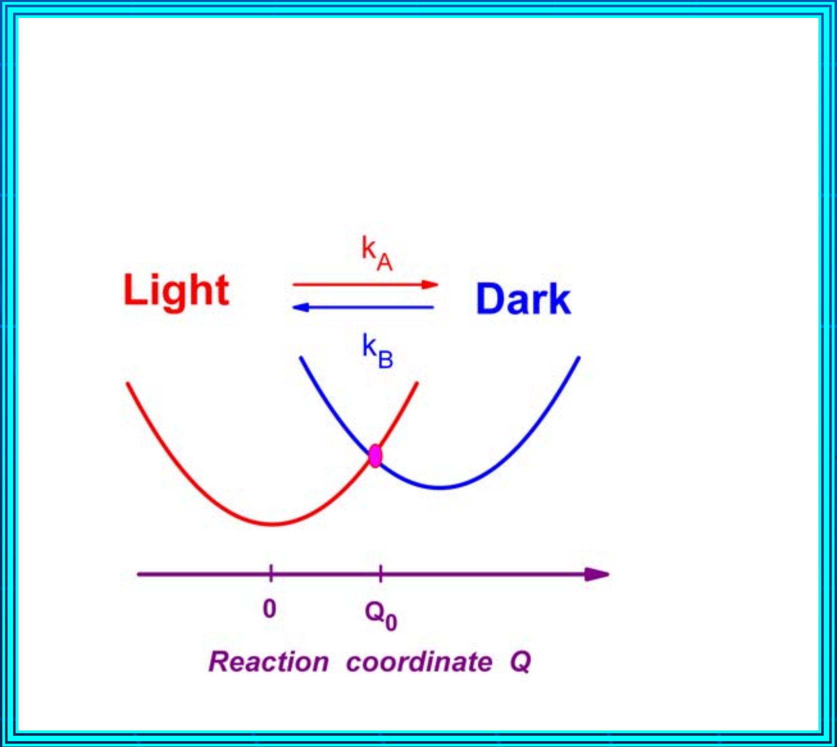


Fluctuations of potential barrier height

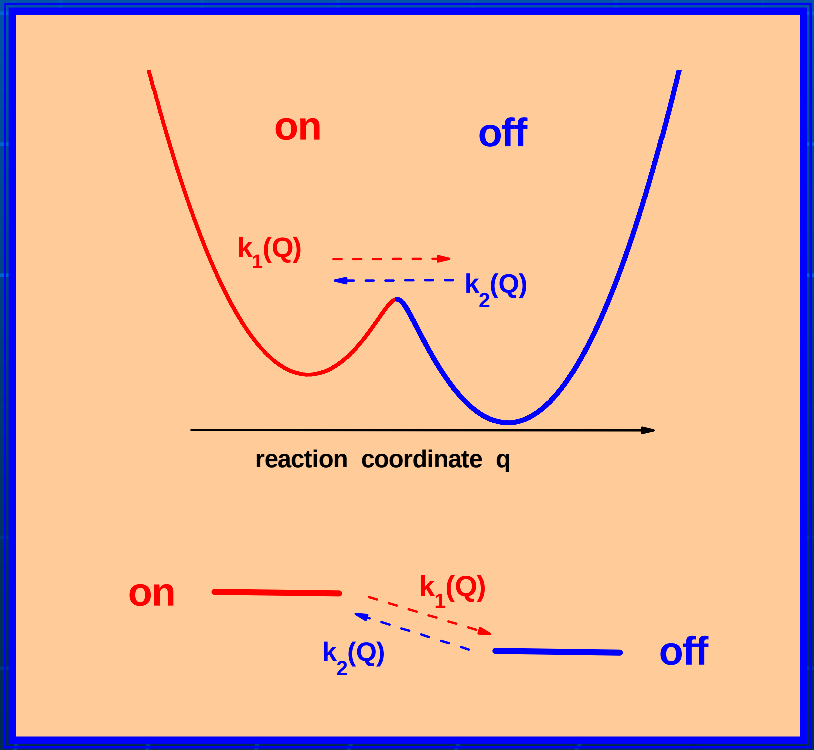
↓

Non-exponential blinking statistics

Charge transfer reactions



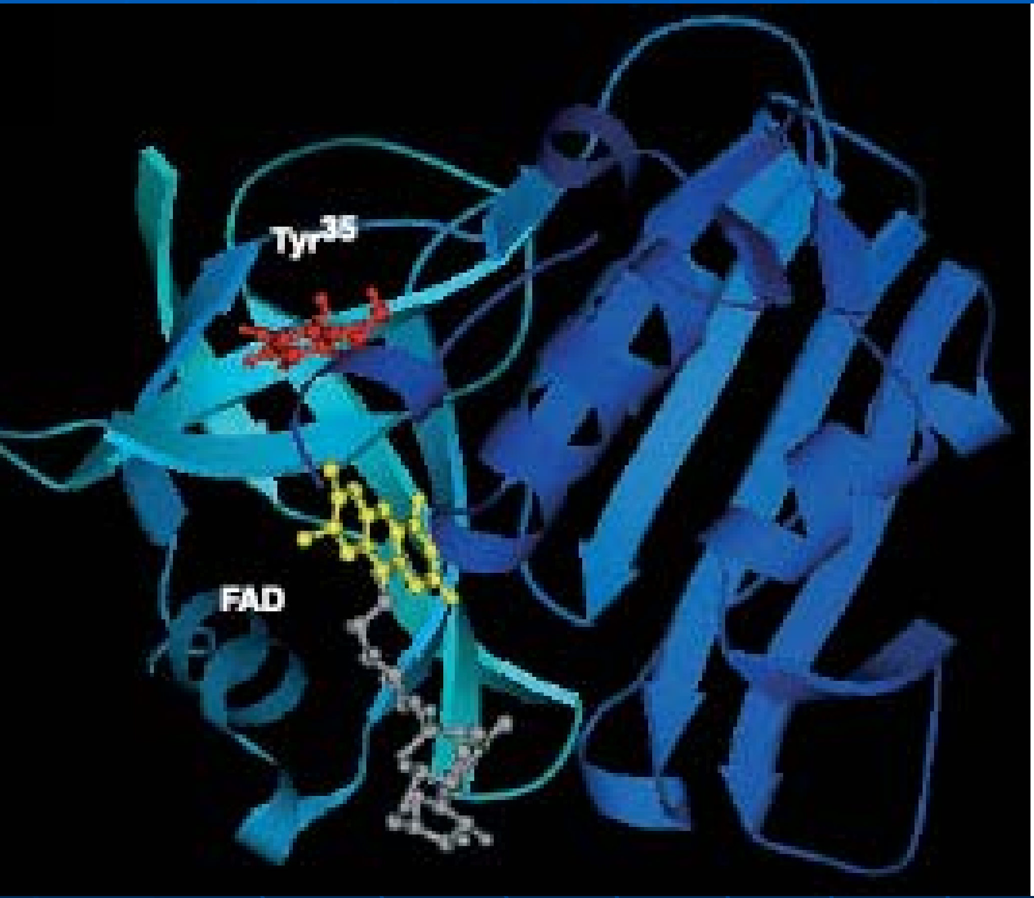
Catalytic reactions

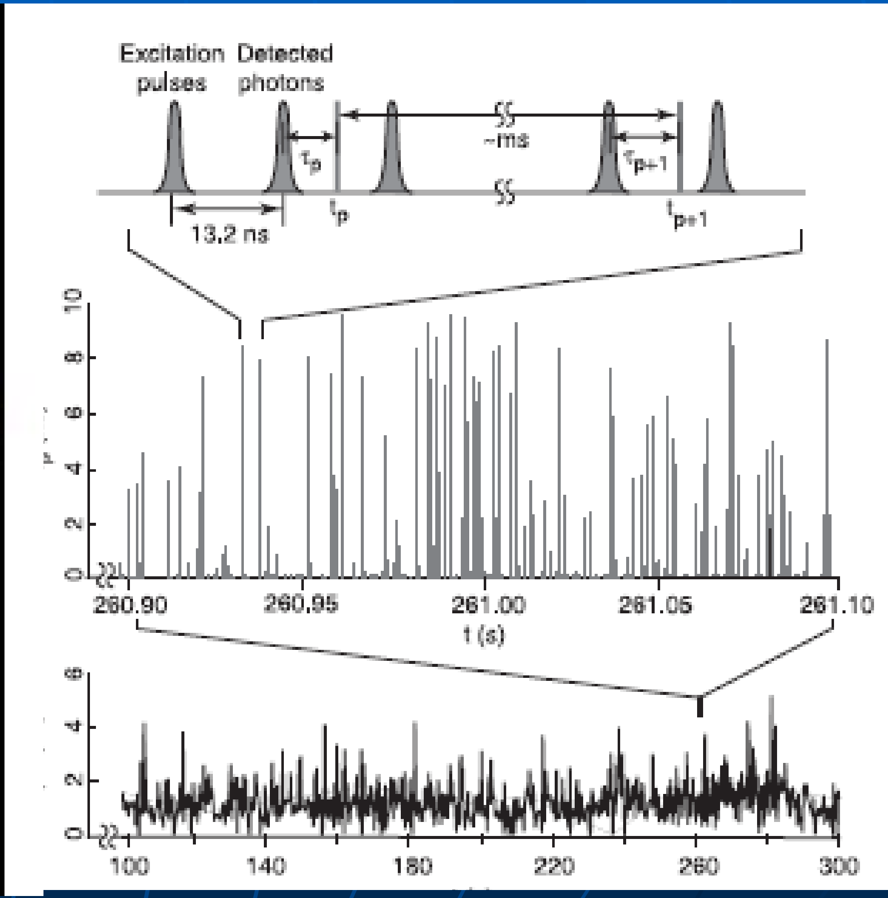


Fluctuating electron transfer rates in single protein molecules

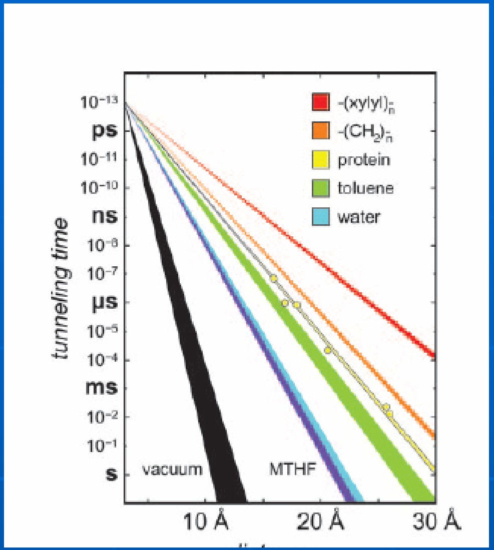
Fre/FAD complex

H. Yang *et al.* *Science* 302, 262 (2003)





Distance-fluctuation model



$$\gamma = \frac{2\pi |V_{ex}|^2}{\hbar\sqrt{4\pi\lambda k_B T}} \exp\left(-\left(\lambda + \Delta G^0\right)^2 / 4\lambda k_B T\right)$$

$$|V_{ex}|^2 \sim \exp(-\beta_{DA}\,\ell(t))$$

If ET is activationless $\Delta G^0 = -\lambda$

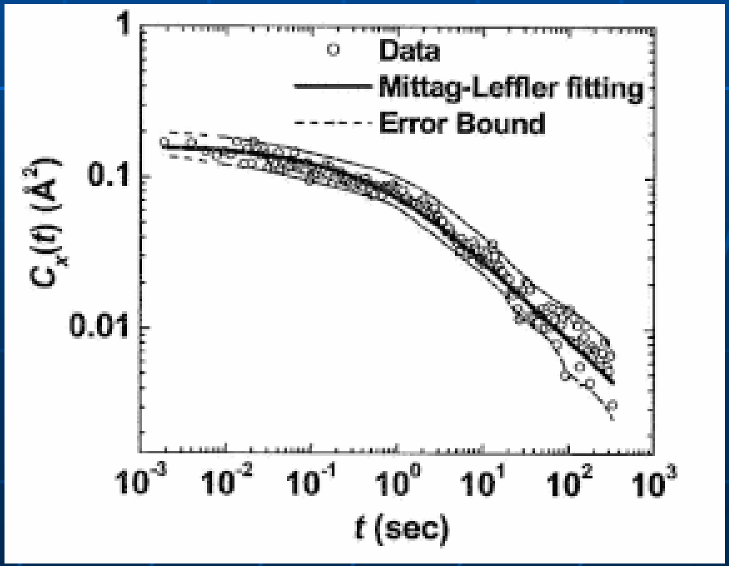
$$ET\ rate \sim \exp(-\beta_{DA}\,\ell)$$

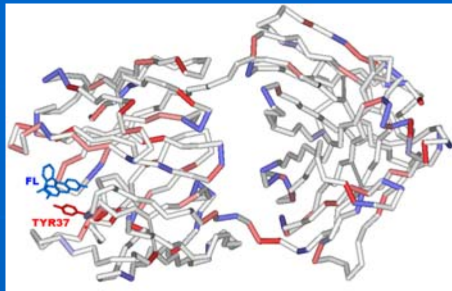
$$C_2(t) \equiv \left\langle \delta\gamma^{-1}(t)\delta\gamma^{-1}(0)\right\rangle \Big/ \left\langle \gamma^{-1}(t)\right\rangle\left\langle \gamma^{-1}(0)\right\rangle$$

$$C_2(t) \equiv \exp\left(\beta^2 C_Q(t)\right) - 1$$

$$C_Q(t) \equiv \left\langle \delta\ell(t)\,\delta\ell(0)\right\rangle,$$

$$\delta\ell(t) = \ell(t) - \left\langle \ell(t)\right\rangle$$



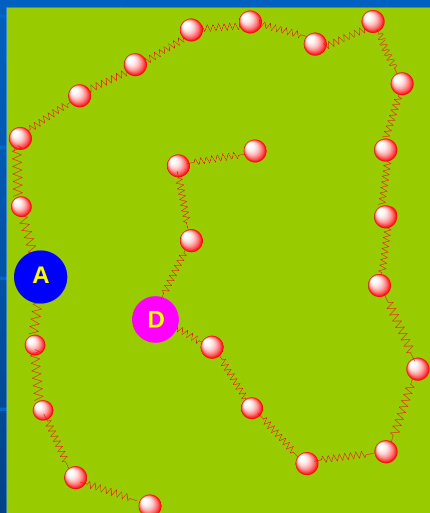


Distance-fluctuation model of a Rouse chain

J. Tang and R. A. Marcus, PR E (2006)

Polymer, DNA, protein

- Neutron scattering, NMR

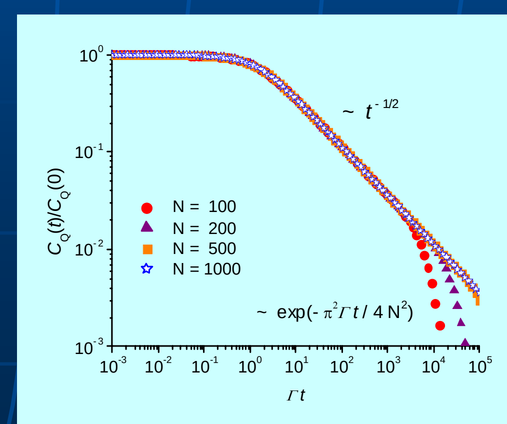


$$\frac{d}{dt}\begin{pmatrix} Q_0 \\ Q_1 \\ \vdots \\ Q_{N-1} \end{pmatrix} + \frac{\omega^2}{\varsigma}\begin{pmatrix} 1 & -1 & 0 & 0 & & & \\ -1 & 2 & -1 & 0 & & & \\ 0 & -1 & 2 & -1 & & & \\ 0 & 0 & -1 & 2 & & & \\ & & & & \ddots & & \\ & & & & & -1 & 0 \\ & & & & -1 & 2 & -1 \\ & & & & 0 & -1 & 1 \end{pmatrix}\begin{pmatrix} Q_0 \\ Q_1 \\ \vdots \\ Q_{N-1} \end{pmatrix} = \begin{pmatrix} F_0(t)/m\gamma \\ F_1(t)/m\gamma \\ \vdots \\ F_{N-1}(t)/m\gamma \end{pmatrix}$$

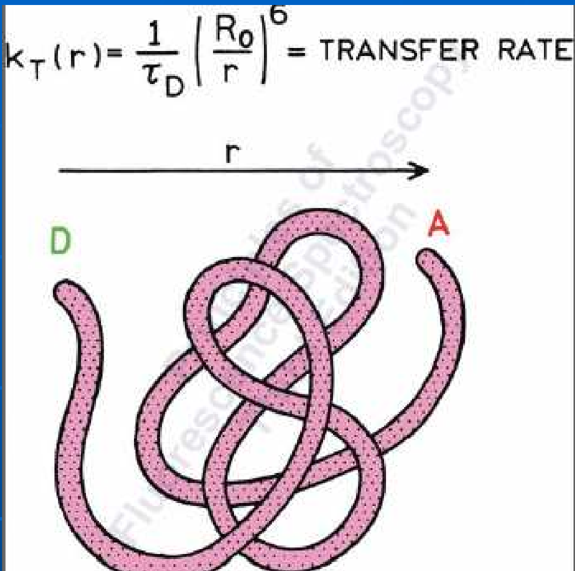
$$\zeta \frac{d}{dt}\mathbf{Q}(t) + \omega^2 \boldsymbol{R}\mathbf{Q}(t) = F(t)/m$$

$$\left\langle F_i^{\mu}(t) \right\rangle = 0 \qquad \left\langle F_i^{\mu}(t) q_j^{\nu}(t) \right\rangle = 0$$

$$\left\langle F_i^{\mu}(t) F_j^{\nu}(\tau) \right\rangle = 2mk_B T\zeta\, \delta(t-\tau)\, \delta_{ij}\delta^{\mu\nu}$$

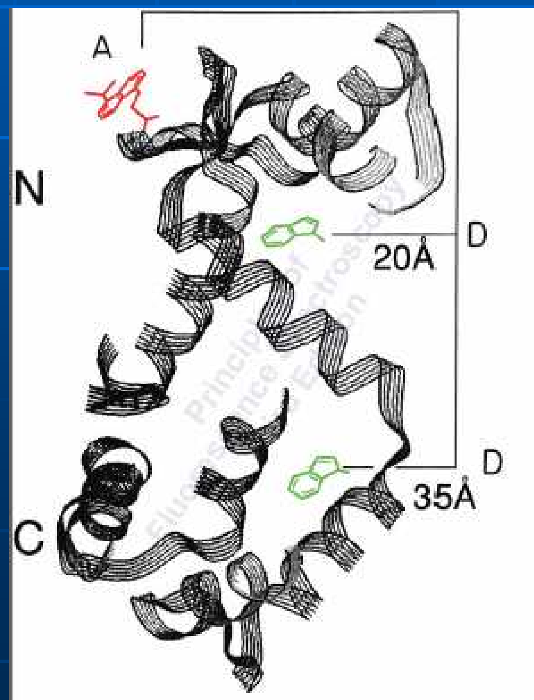


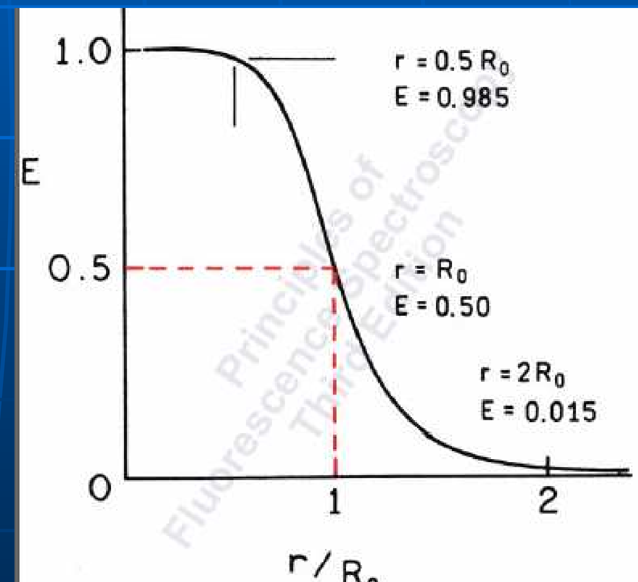
Förster's Fluorescence resonance energy transfer (FRET)



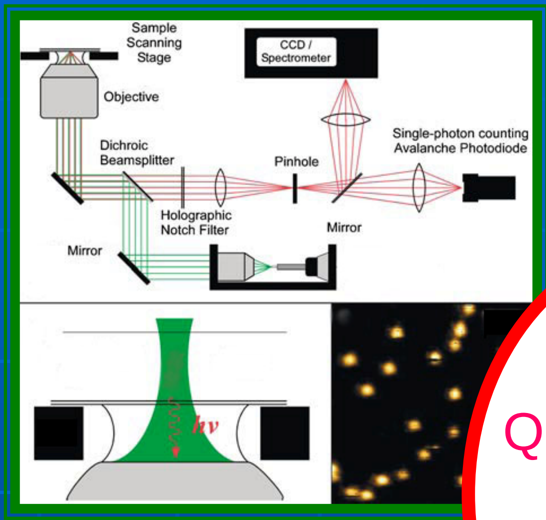
Efficient of energy transfer

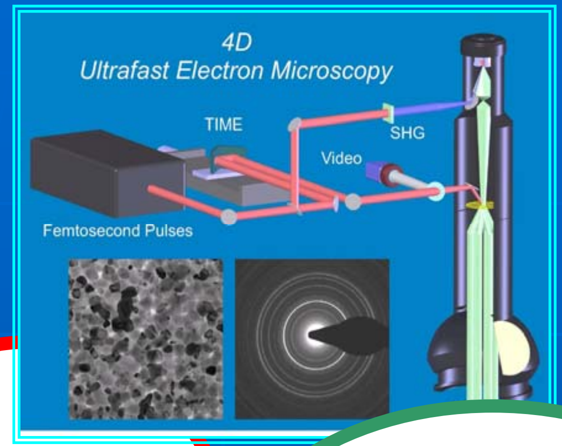
$$E = \frac{k_T(r)}{\tau_D^{-1} + k_T(r)}$$





Spinach calmodulin
D: tryptophan
A: AEDANS





Quantum dots,
Nanorods,
Biomolecues

Photochemistry,
Photovoltaics

Light-induced
phase transitions

Protein dynamics &
Biomed applications