

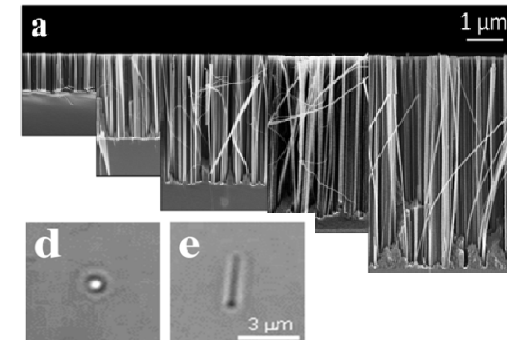
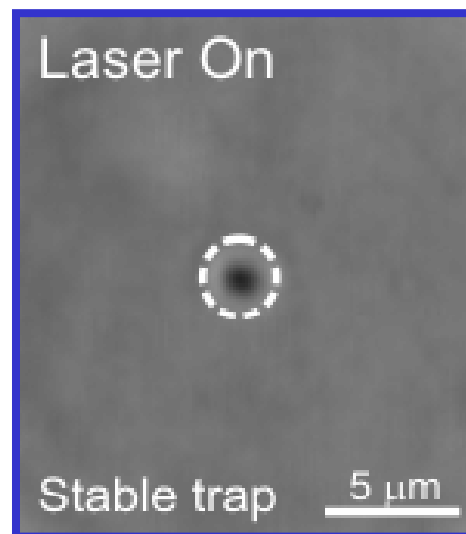
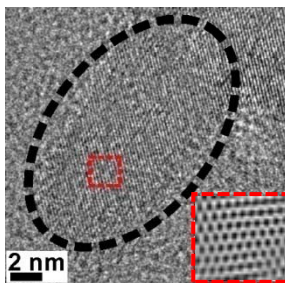
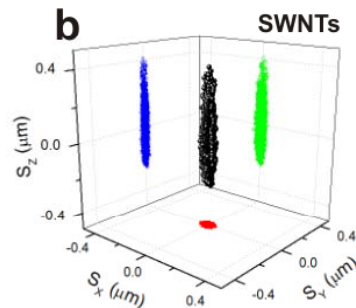
Optical Trapping of Nanostructures

Femtonewton Force Sensing and Ultra-sensitive Spectroscopy

Onofrio M. MARAGÒ

CNR-IPCF, Istituto per i Processi Chimico-Fisici (Messina, Italy)

marago@me.cnr.it



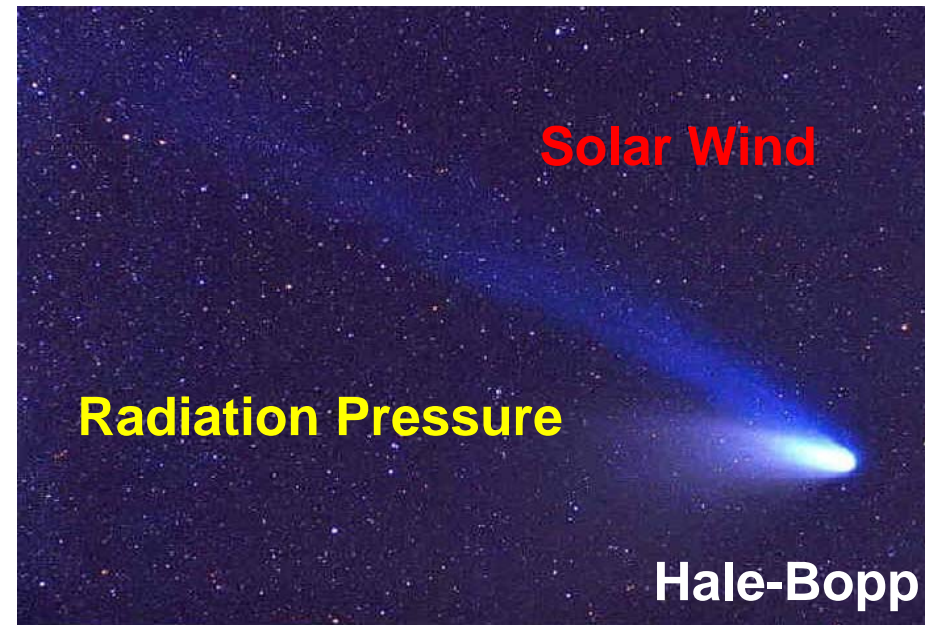
NanoSpain
Conf 2012

FEBRUARY 27 - MARCH 01, 2012
SANTANDER (SPAIN)

Outline

- Optical Trapping & Force sensing
- OT of Linear Nanostructures (SWNTs & SiNW)
 - *Brownian motion & Force sensing*
 - *Size-scaling*
 - *Optical Binding*
- OT & Raman OT of Graphene
- Plasmon-Enhanced Forces & Spectroscopy
 - *SERS Tweezers*
 - *Optical Forces on Hybrid Nanostructures, Nanoswimmers*
- Conclusions

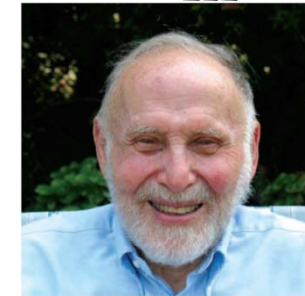
- **J Kepler (1610)**
comet tails are the result of light pressure



- **J C Maxwell (1864)**
light pressure is explained in electromagnetic theory
- **P Lebedev (1901)**
measures light pressure for the first time
- **A Ashkin, T Haensch & A Schawlow (1970s)**
first proposals to manipulate atoms and microparticles, laser cooling
- **A Ashkin & S Chu (1986)**
at Bell Laboratories moves and traps latex spheres suspended in water using a focused laser beam. **Optical Tweezers** are born!

A light touch NATURE PHOTONICS | VOL 5 | JUNE 2011 | www.nature.com/naturephotonics

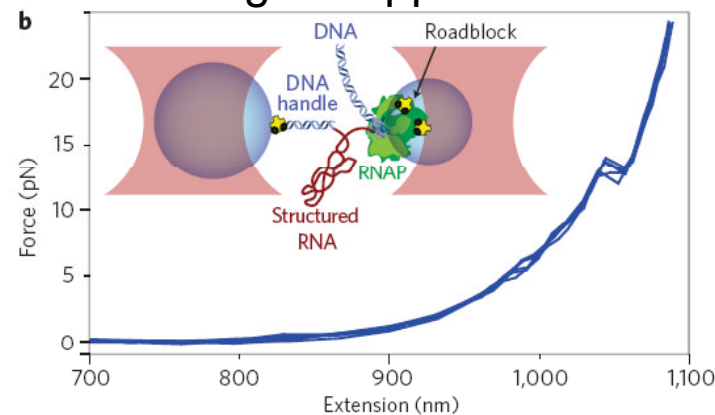
Since the discovery of the optical gradient force in 1970 and the first use of laser beams to manipulate microscopic and atomic systems in 1986, optical manipulation has proved to be a versatile optical tool for uncovering mysteries throughout many fields of science.



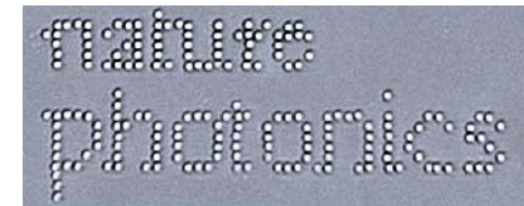
Arthur Ashkin



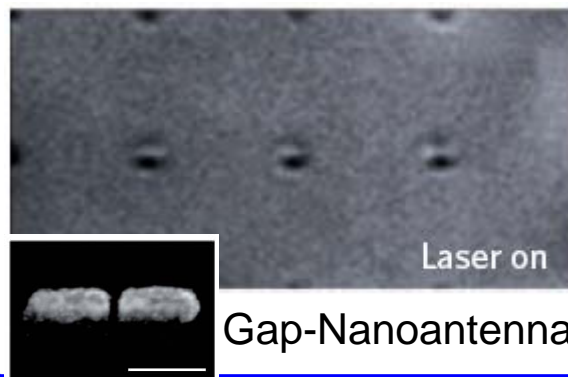
Biological Applications



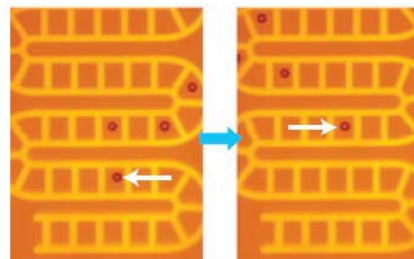
Holographic Tweezers



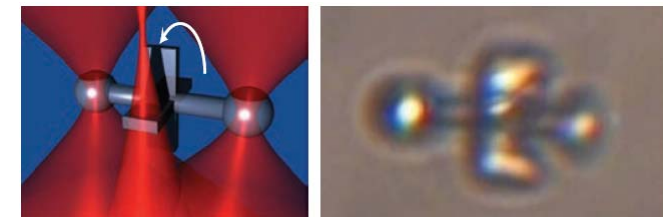
Optical NanoTweezers



Optoelectronic Tweezers



Optofluidics & Lab-on-Chip



Optical trapping of particles is a consequence of the radiation force that stems from the conservation of electromagnetic momentum.

Rayleigh Regime, $d/\lambda \ll 1$

- Force divides into two components: gradient force and the scattering force

Ray Optics Regime, $d/\lambda \gg 1$

- Microsphere acts like a lens
- Trapping forces from reflection and refraction of rays
- Forces proportional to gradient of intensity

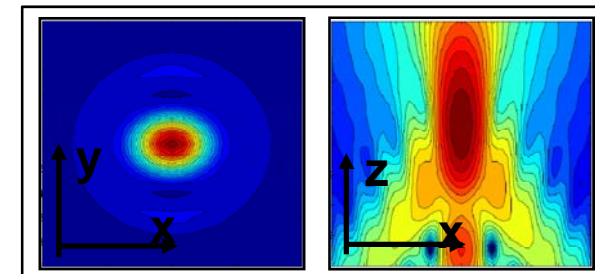
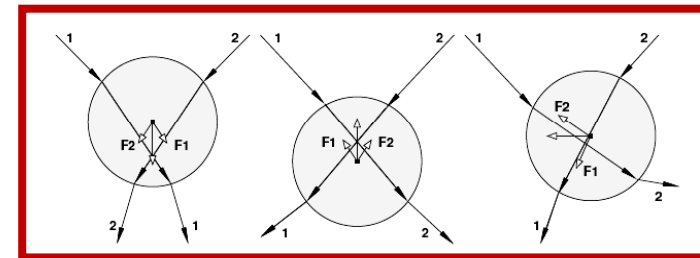
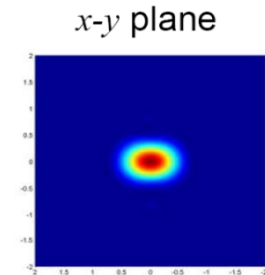
Complex Region, $d/\lambda \approx 1$

- Full electromagnetic Theory
- Vector character of laser field
- Make use of Transition-Matrix approach
- **Extension to non-spherical particles!**

$$U_{\text{dip}} = -\underline{p} \cdot \underline{E}$$

$$\underline{F}_{\text{grad}} = -\underline{\nabla} U_{\text{dip}}$$

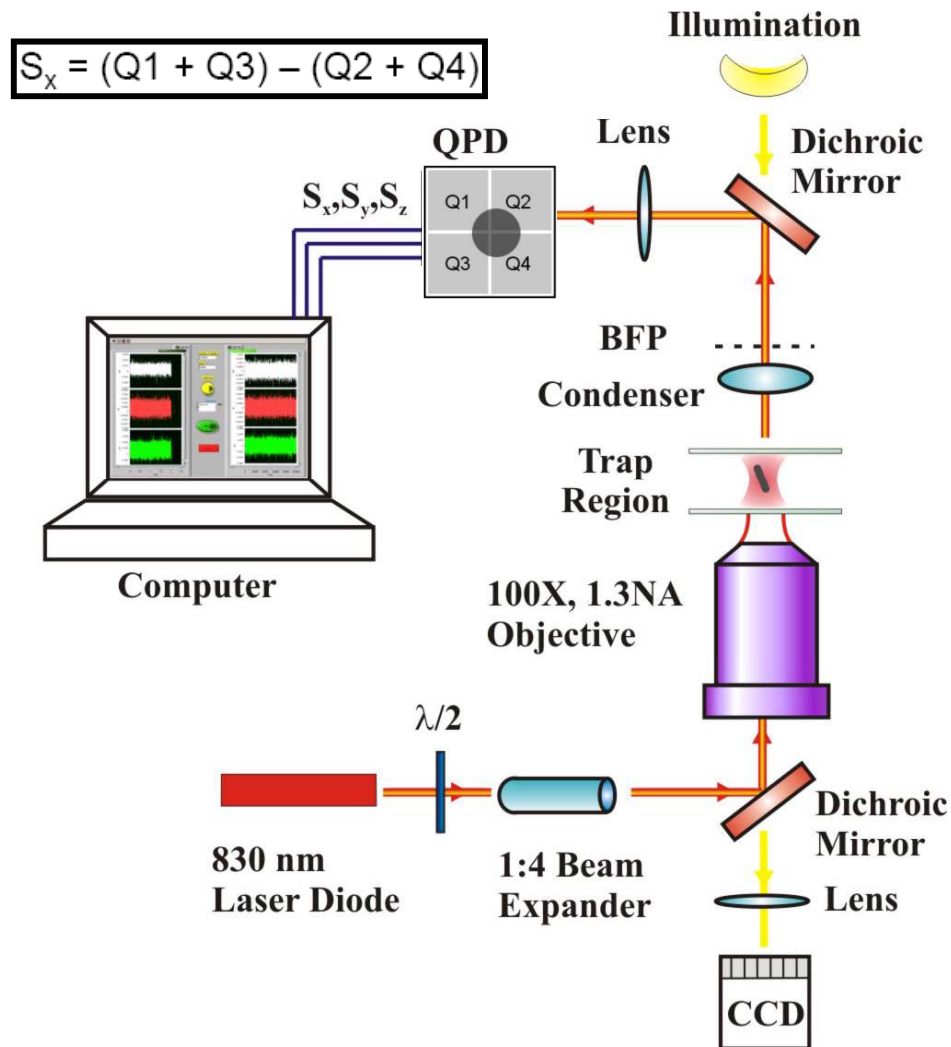
$$\propto \underline{\nabla} I(\underline{r}) = -\kappa_i x_i$$



$$\underline{F}_{\text{Rad}} = r'^2 \int_{\Omega'} \hat{\mathbf{r}}' \cdot \langle \mathbf{T}_M \rangle d\Omega'$$



Optical Tweezers & Force Sensing



- Standard OT with QPD forward or back detection
- Multiwavelength: 830nm (150mW), 785nm (80mW), 633nm (17mW), 417nm (30mW)
- Radial Polarizer (arcoptics)
- Piezostage (1nm resolution)
- Galvomirrors

Back focal plane interferometry combined with a QPD is sensitive to Brownian fluctuations

Brownian motion is a key ingredient in Force Sensing with optical tweezers.

- Equation of motion of a damped harmonic oscillator subject to a randomly fluctuating force:

$$m \cancel{\frac{d^2x}{dt^2}} + \gamma \frac{dx}{dt} + \kappa x = \xi(t)$$

Stokes

Trap

- The term $\xi(t)$ describes random (uncorrelated) fluctuations in force with zero mean, i.e.

$$\langle \xi(t) \rangle = 0 \quad \langle \xi(t + \tau) \xi(t) \rangle = \frac{2k_B T}{\gamma} \delta(\tau)$$

- Equation of motion in the overdamped regime:

$$\gamma \partial_t x(t) = -\kappa x(t) + \xi(t)$$

- Calculate the **autocorrelation** of position fluctuations:

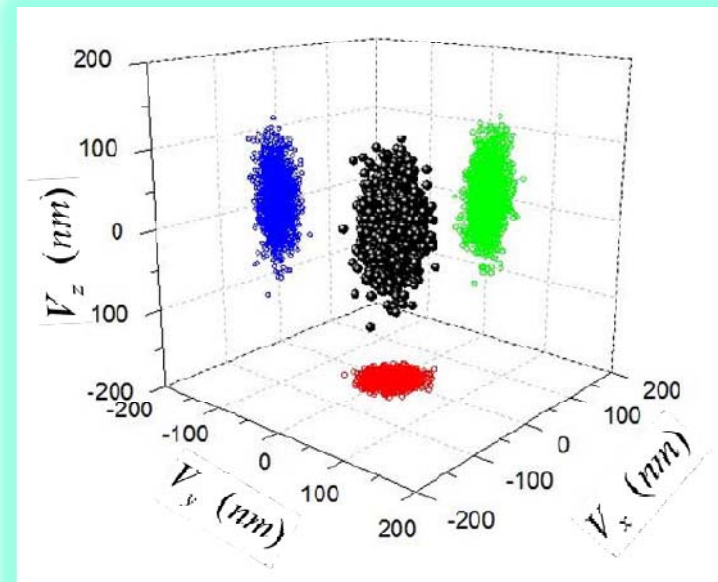
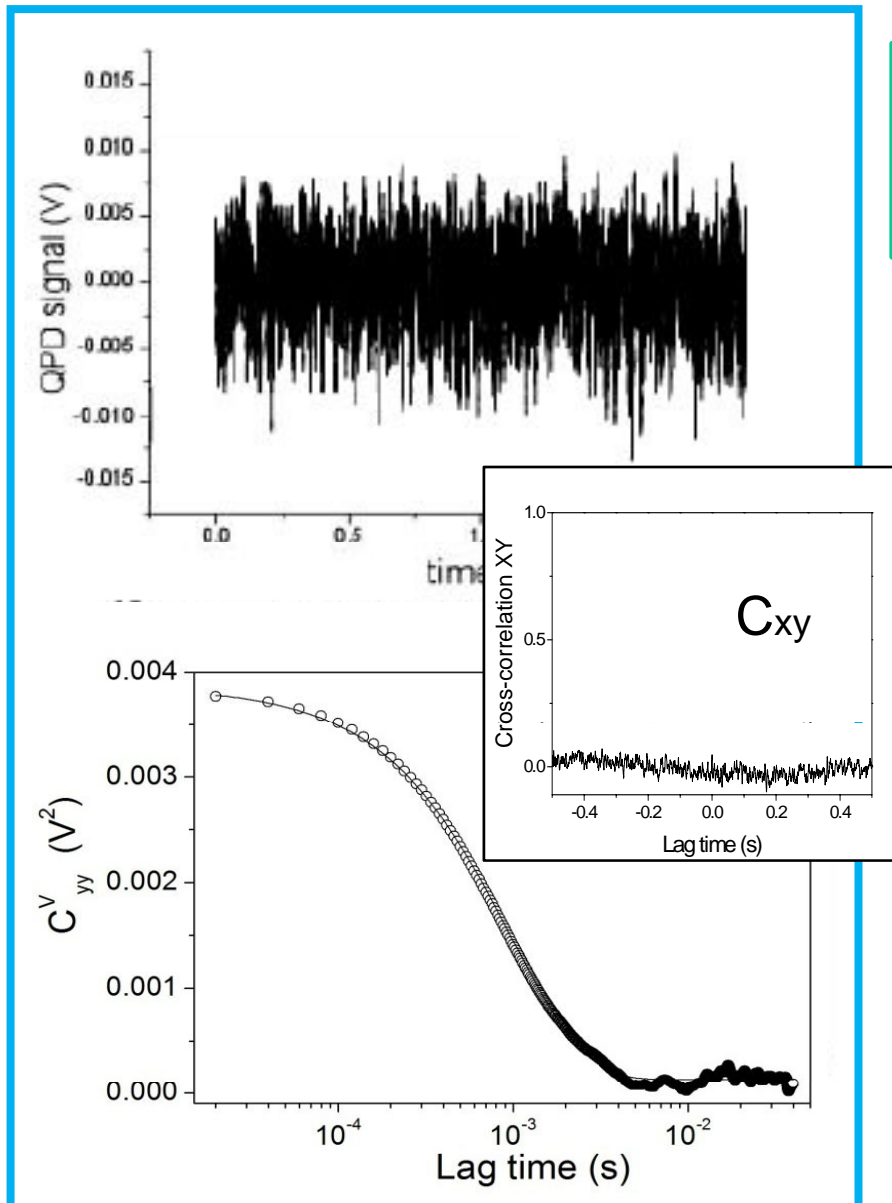
$$C_{xx}(\tau) = \langle x(t)x(t + \tau) \rangle$$

- The solution to which is straightforward:

$$C_{xx}(\tau) = C_{xx}(\tau = 0) \exp(-\omega \tau)$$

$$\omega = \frac{\kappa}{\gamma}$$

From QPD tracking signals we get
Autocorrelation Functions and
eventually the Force Constants



Autocorrelation:

Meiners&Quake, PRL (1999)

Meiners&Quake, PRL (2000)

Rohrbach, PRL (2005)

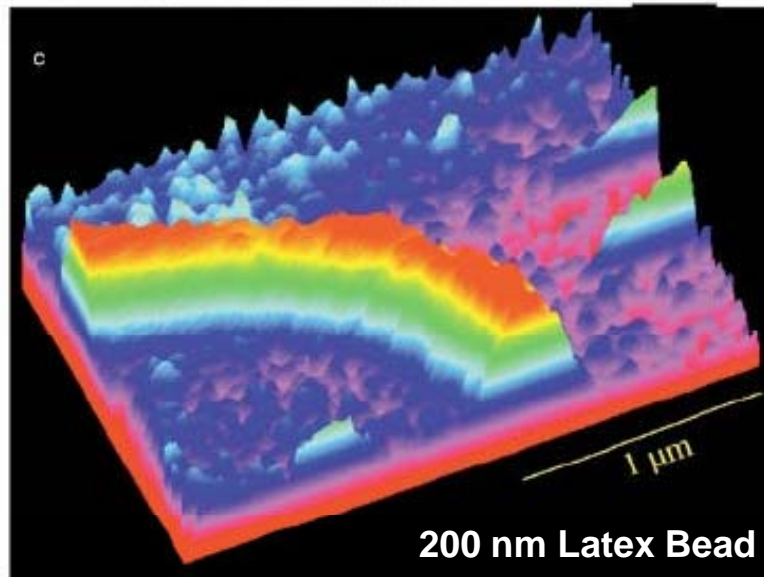
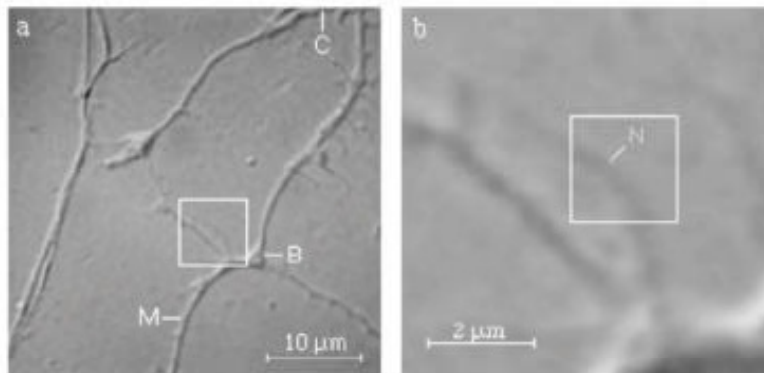
Volpe&Petrov, PRL (2006)



Photonic Force Microscopy

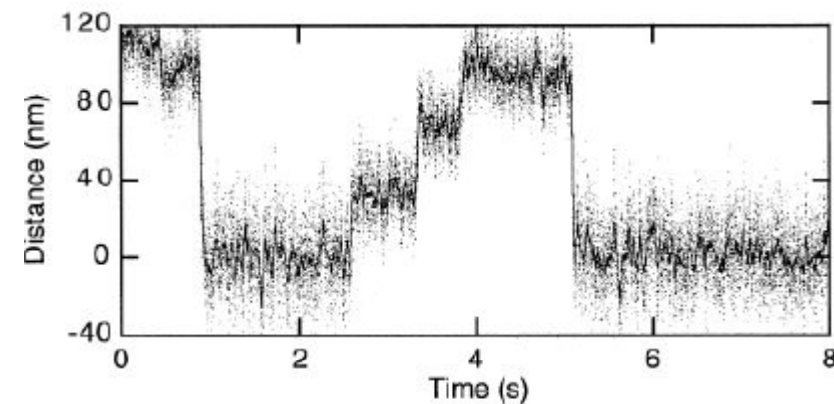
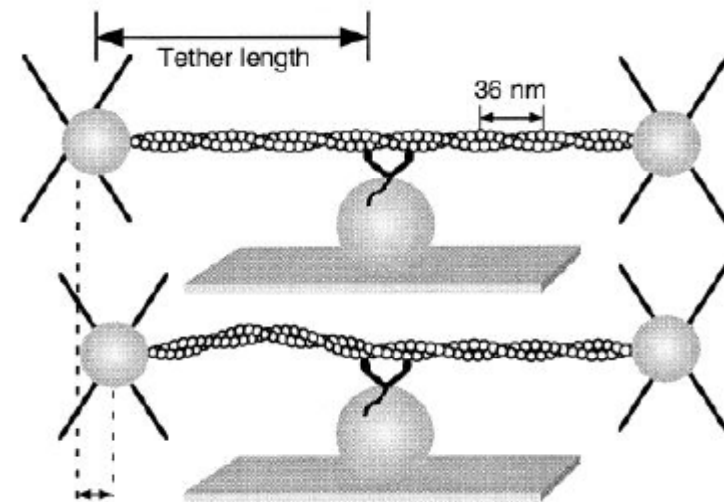


Scanning Probe Technique based on Force Sensing with Optical Tweezers



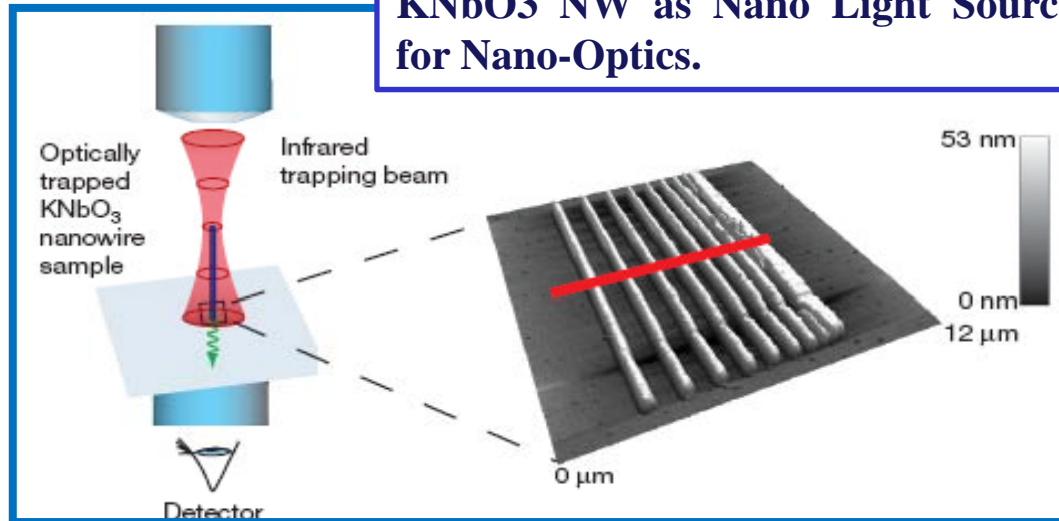
Data from: A. Pralle et al, *Single Mol.* 1 12 (2000)

Dual trap with actin filament
Myosin steps along actin



Data from: A. Mehta et al, *Nature* 400 590 (1999)

KNbO₃ NW as Nano Light Source for Nano-Optics.

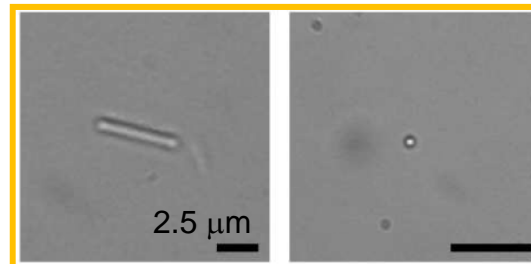
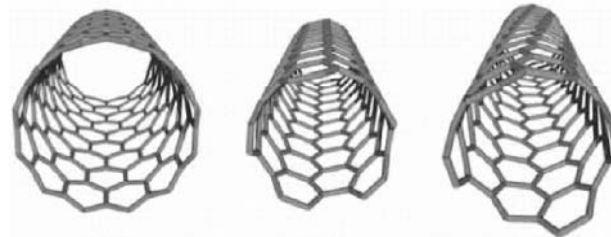


Nanowires:

Agarwal et al., Optics Express (2005)
 Pauzauskie et al., Nat. Mat. (2006)
 Nakayama et al., Nature (2007)
 Borghese et al., Phys. Rev. Lett. (2008)
 Carberry et al., Nanotech. (2010)
 Simpson&Hanna, JOSA A (2010)
 Simpson&Hanna, PR E (2010)
 Reece et al., Nano Lett. (2011)
 Dutta et al., Nano Lett. (2011)
 Irrera et al., Nano Lett. (2011)

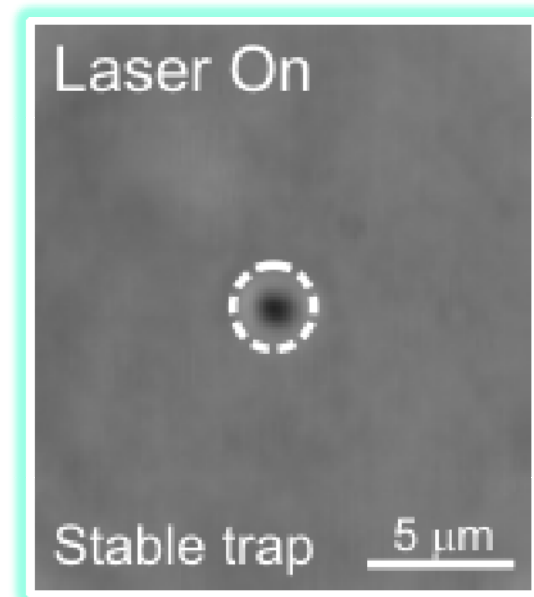
Nanotubes:

Tan et al., Nano Lett. (2004)
 Plewa et al., Optics Express (2004)
 Zhang et al., APL (2006)
 O.M. Maragò et al., Physica E (2008)
 O.M. Maragò et al., Nano Lett. (2008)
 P.H. Jones, et al. ACS Nano (2009)
 Pauzauskie et al, APL (2009)



Nanofibers:

Neves et al., Optics Express (2010)

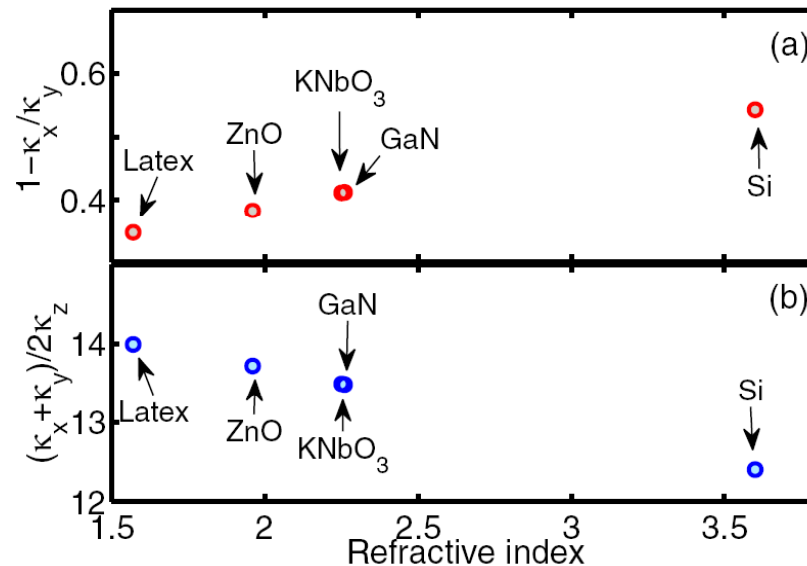


Radiation Force and Torque on non-spherical particles in the T-matrix formalism

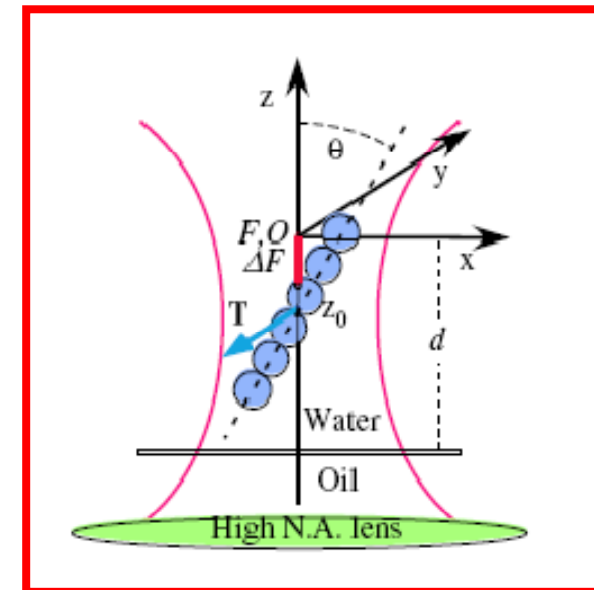
$$\mathbf{F}_{\text{Rad}} = r'^2 \int_{\Omega'} \hat{\mathbf{r}}' \cdot \langle \mathbf{T}_M \rangle d\Omega'$$

$$\mathbf{\Gamma}_{\text{Rad}} = -r'^3 \int_{\Omega'} \hat{\mathbf{r}}' \cdot \langle \mathbf{T}_M \rangle \times \hat{\mathbf{r}}' d\Omega'$$

where $\langle \mathbf{T}_M \rangle$ is the time averaged Maxwell stress tensor



linear nanostructure
 $x_{D/2} \ll 1$ and $x_{L/2} \approx 1$



Polarization and Geometrical asymmetry

$$\kappa_P = 1 - \kappa_x / \kappa_y$$

$$\kappa_G = (\kappa_x + \kappa_y) / (2\kappa_z)$$

Singer et al., Phys Rev E (2006); [Borghese et al., Optics Express, \(2007\)](#); [Borghese et al., Phys Rev Lett \(2008\)](#);
 Bareil & Sheng, Opt. Express (2010); Simpson & Hanna, Phys Rev E (2010);

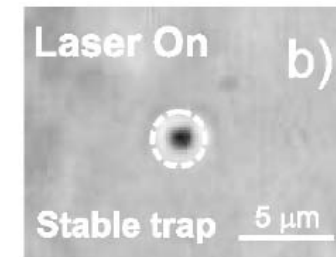
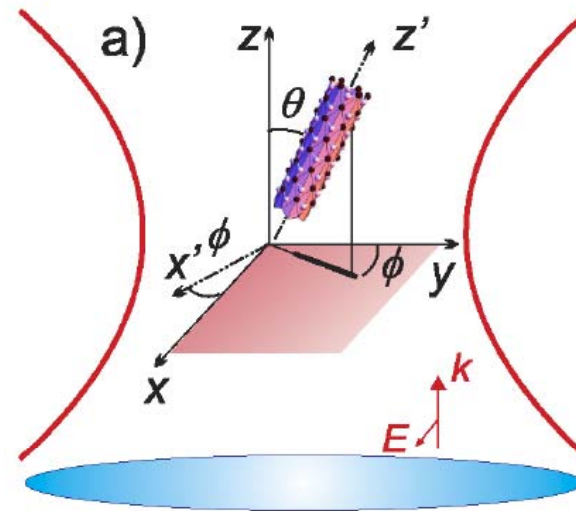
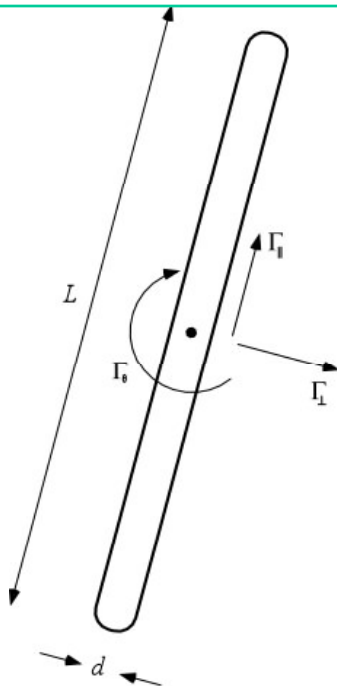
[S. Albaladejo, J.J. Sáenz, M.I. Marqués Nano Lett., 2011, 11,4597–4600 \(Nano Sail\)](#)

Broersma, J.Chem.Phys. (1981);
Tirado et al. J. Phys Chem C(1984)

Hydrodynamics of a rod-like nanostructure is anisotropic

$$\Gamma_{\perp} = \frac{\ln p + \delta_{\perp}}{4\pi\eta L}, \quad \Gamma_{\parallel} = \frac{\ln p + \delta_{\parallel}}{2\pi\eta L}$$

$$\Gamma_{\Theta} = \frac{3(\ln p + \delta_{\Theta})}{\pi\eta L^3}$$



The signals from the QPD are a composition of center of mass X_i and angular motion Θ_i .

$$S_x \sim \beta_x (X + a \Theta_x); \quad S_y \sim \beta_y (Y + b \Theta_y); \quad S_z \sim \beta_z Z$$

Small angle approximation

Brownian Motion is more complex

$$\begin{aligned}\partial_t X_i(t) &= -\omega_i X_i(t) + \xi_i(t), \quad i = x, y, z \\ \partial_t \Theta_j(t) &= -\Omega_j \Theta_j(t) + \xi_j(t), \quad j = x, y\end{aligned}$$

From correlation functions we can extrapolate the force and torque constants on the SWNT bundle

$$\begin{aligned}C_{X_i X_i}(\tau) &= \langle X_i(t) X_i(t + \tau) \rangle \\ C_{\Theta_j \Theta_j}(\tau) &= \langle \Theta_j(t) \Theta_j(t + \tau) \rangle\end{aligned}$$

$$\begin{aligned}\omega_x &= \Gamma_{\perp} k_x, \quad \omega_y = \Gamma_{\perp} k_y, \quad \omega_z = \Gamma_{\parallel} k_z \\ \Omega_x &= \Gamma_{\Theta} k_{\Theta_x}, \quad \Omega_y = \Gamma_{\Theta} k_{\Theta_y}.\end{aligned}$$

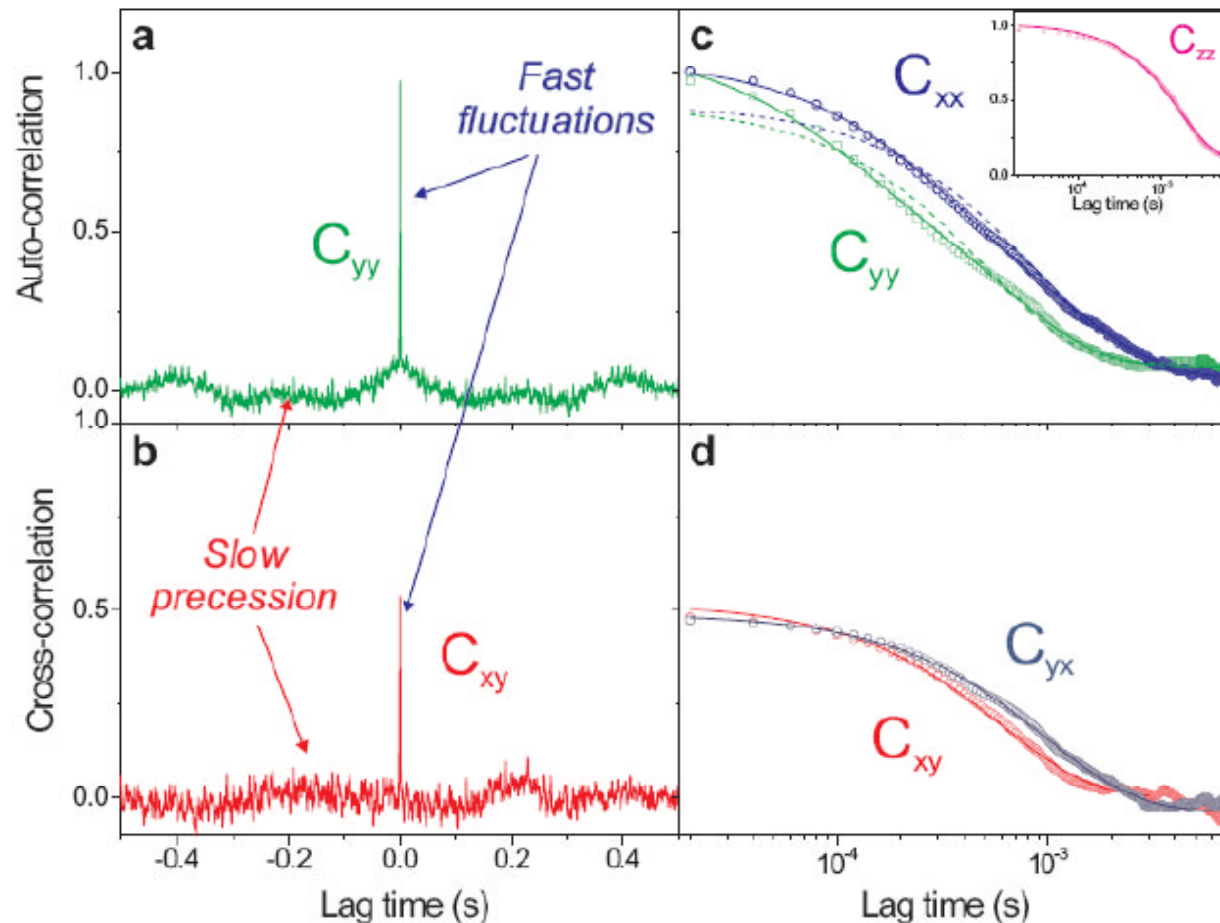
Relaxation Frequencies for
Translational and Angular Motion

Hydrodynamics of a rod-like nanostructure
is embedded in the relaxation frequencies

Correlation functions of the tracking signals give information on torque and force constants.

$$C_{ii}(\tau) = \langle S_i(t) S_i(t + \tau) \rangle$$

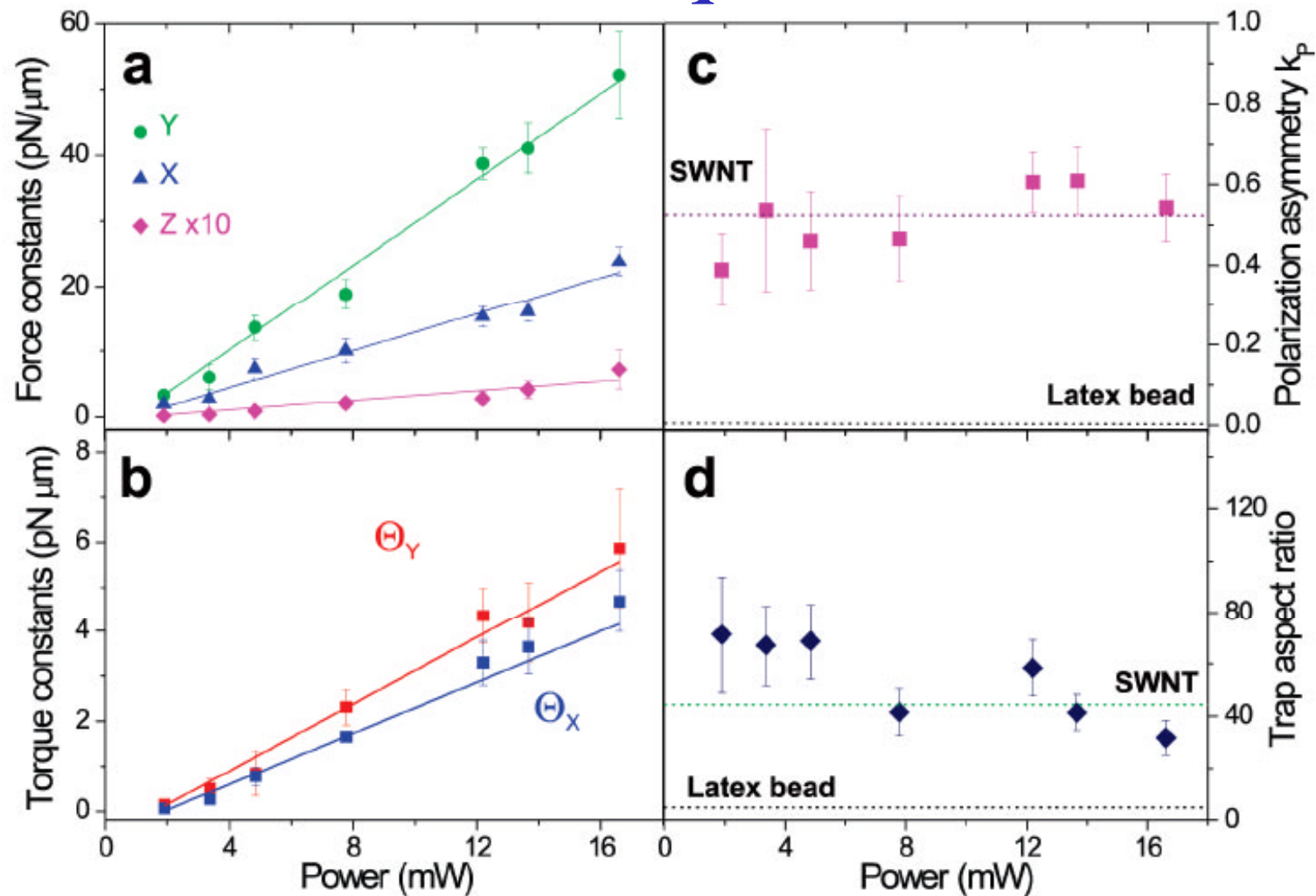
$$C_{xy}(\tau) = \langle S_x(t) S_y(t + \tau) \rangle$$



*Double Exp for
"fast" dynamics*

*Simple Exp for
Z and Cross*

Non-conservative forces:
Simpson&Hanna, PR E (2010)

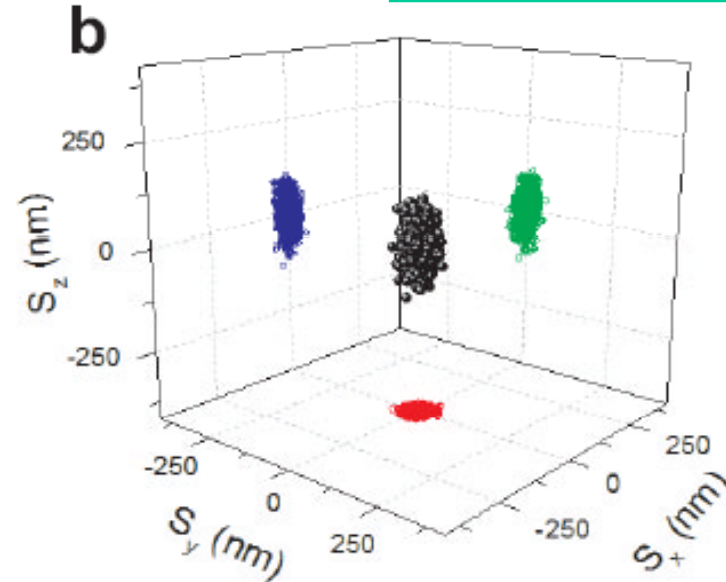
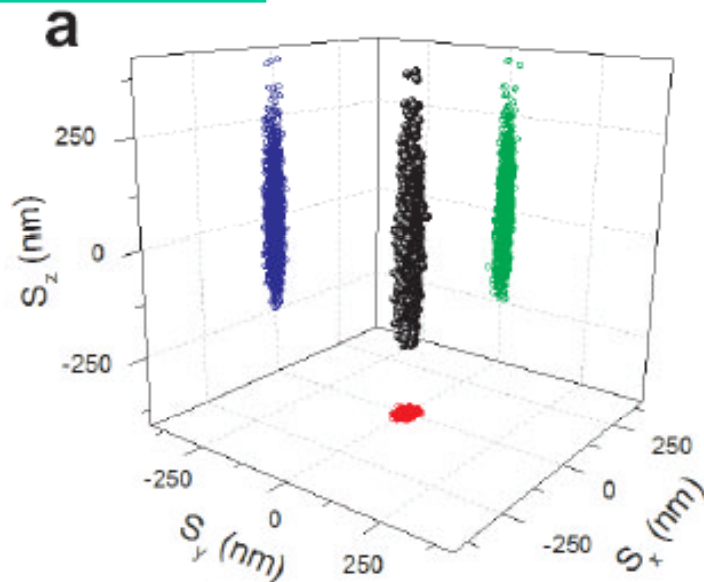


FemtoNewton Regime!

Polarization and Geometrical asymmetry are consistent with OT theory of linear nanostructures

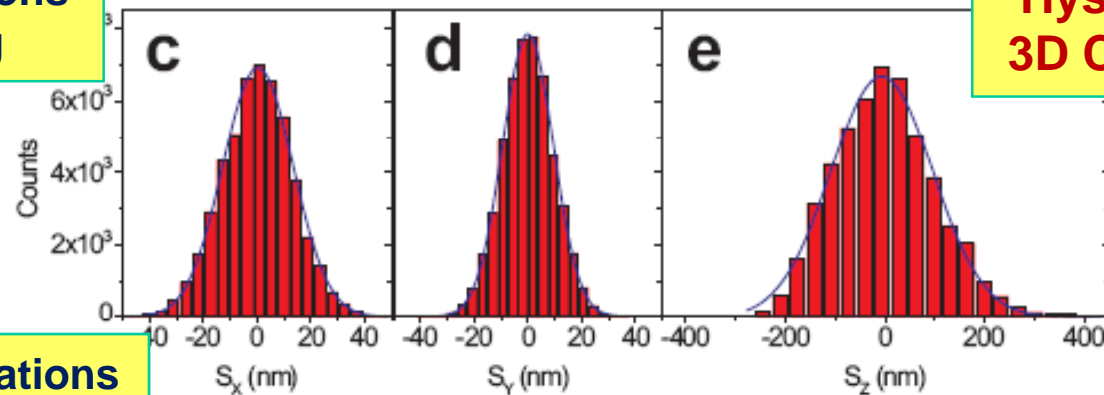
SWNT bundle

Latex Bead 2um



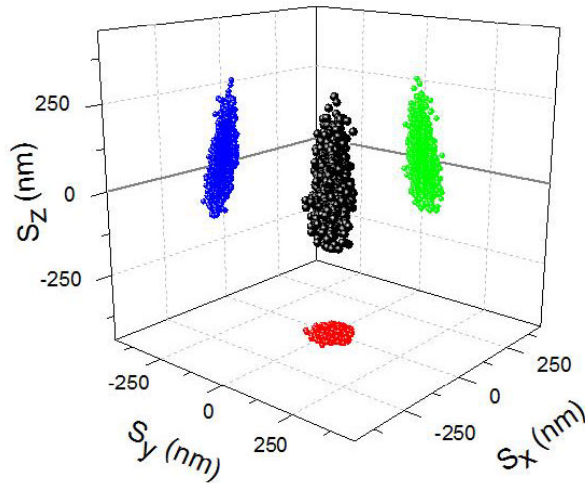
**Angular fluctuations
within 1-2 deg**

**Histograms of
3D CNTtracking**

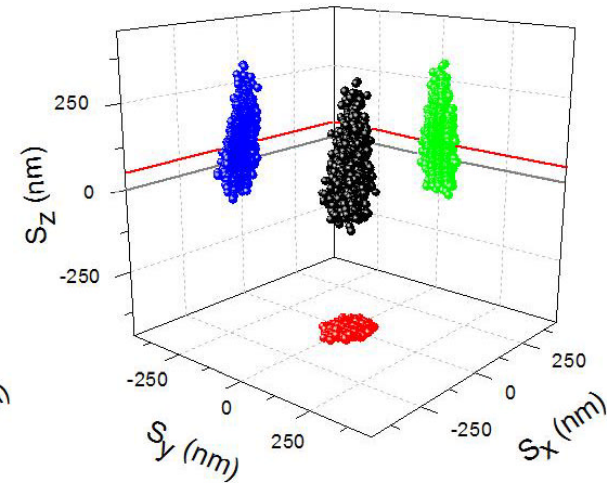
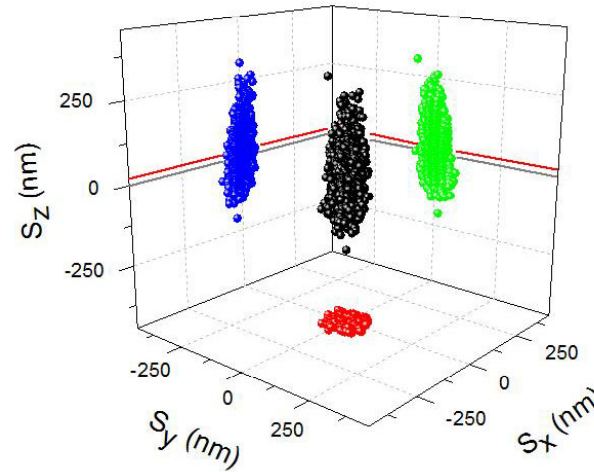


**Transverse fluctuations
in the 10 nm range**

Trapping with 830nm



Pushing with blue 417nm @ low power



$$\Delta z = 19 \pm 2 \text{ nm}$$

$$F_{\text{blue}} = k_z \Delta z = 16 \pm 3 \text{ fN}$$

$$P_{\text{blue}} = 170 \text{ } \mu\text{W}$$

$$\Delta z = 44 \pm 3 \text{ nm}$$

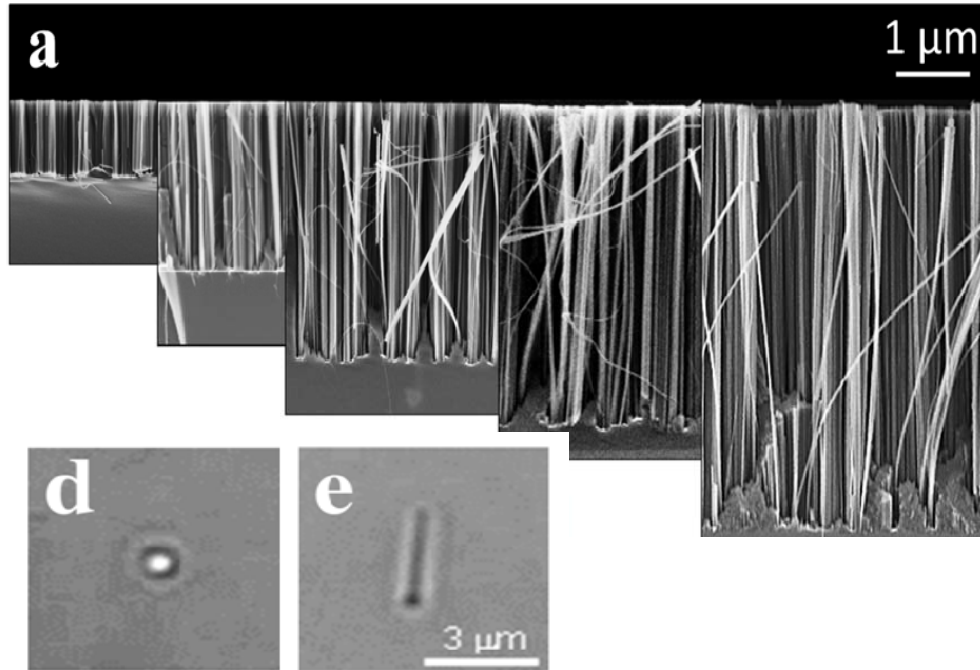
$$F_{\text{blue}} = 45 \pm 9 \text{ fN}$$

$$P_{\text{blue}} = 550 \text{ } \mu\text{W}$$

Uncertainty due to
Nanotube Length

FemtoNewton Regime!

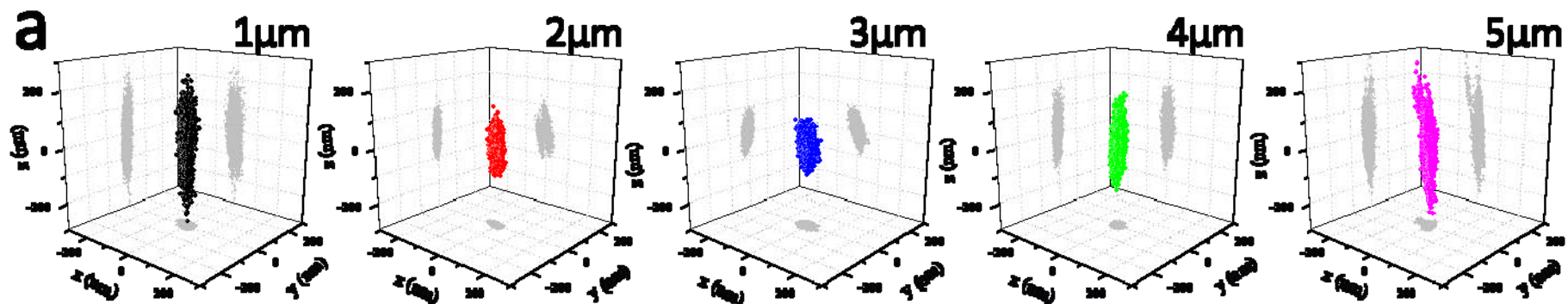
$$C_{\text{ext}} = cF/nI_0 = 1100 \pm 200 \text{ nm}^2$$



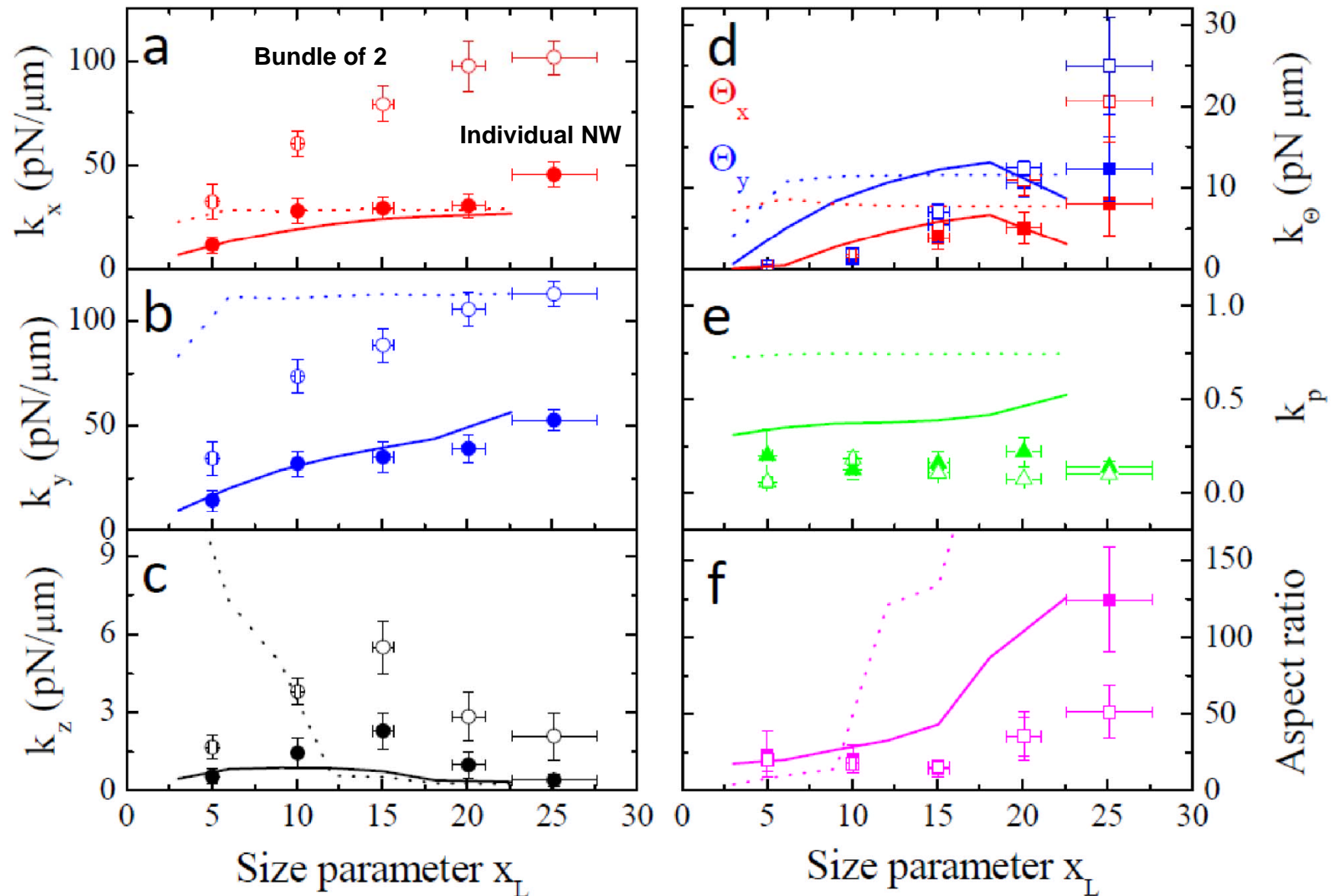
We can now control the length and the diameter

Length controls optical forces and torques

Size-scaling with the size parameter $x_L = \pi n L / \lambda$

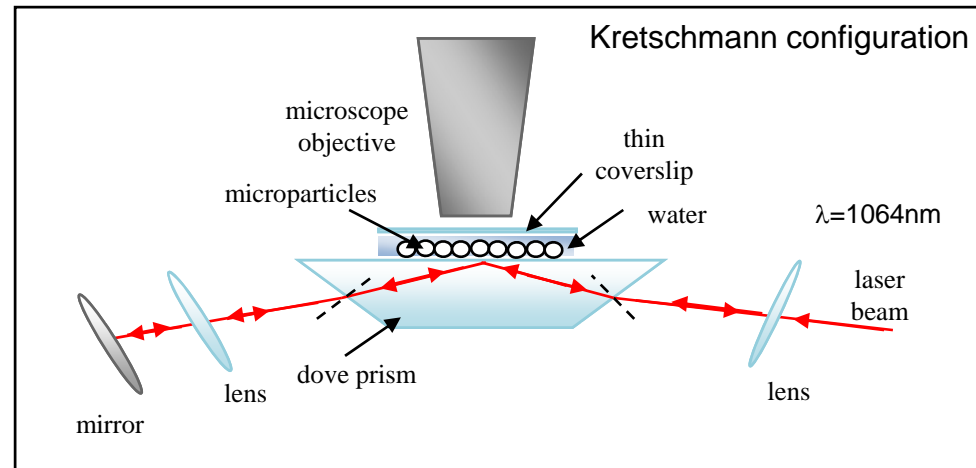


Similar behaviour as for nanotube bundles but controlled size



(Collaboration with P.H. Jones, UCL)

Optical binding forces arise in the presence of multiple particles. These particles scatter the incoming light and the scattered light induce optical forces on the nearby particles.



- Nanotubes align end-to-end with **k-vector** of the evanescent standing wave
- Polarization of evanescent field has no effect on alignment

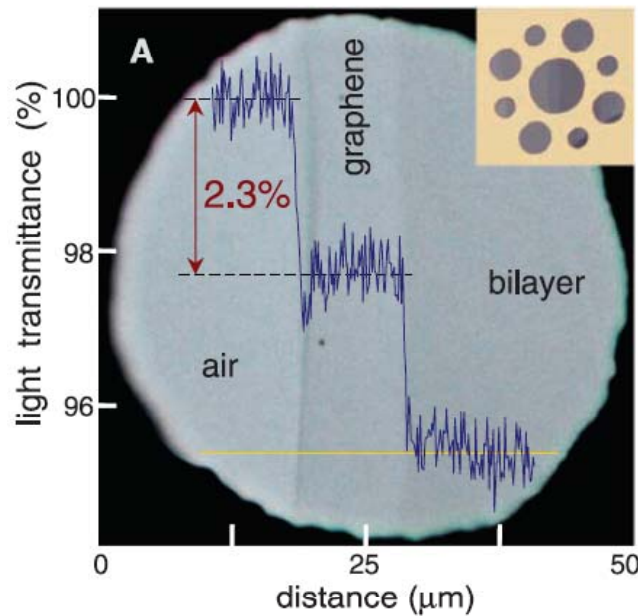
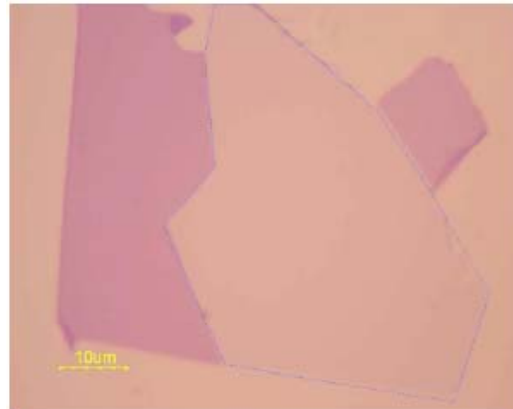
Nobel Prize
2010!



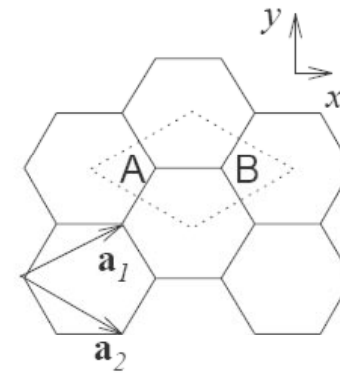
A. Geim



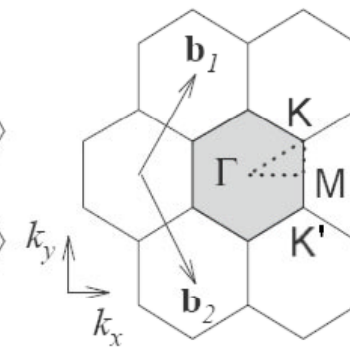
K. Novoselov



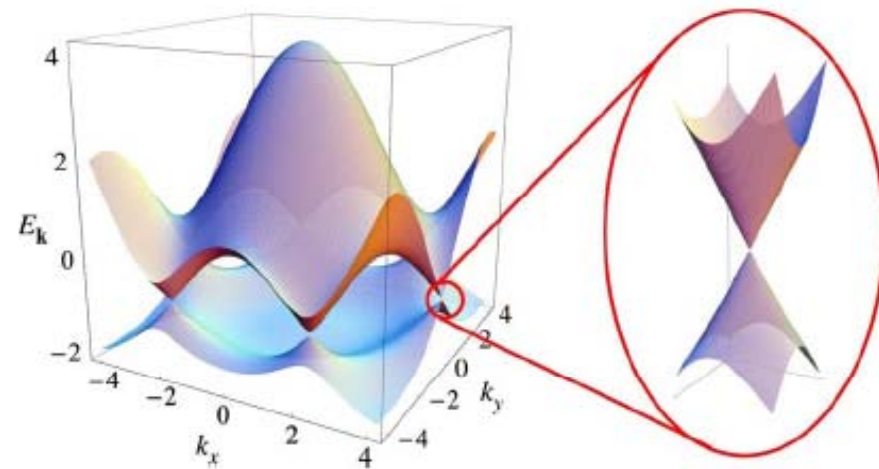
Novoselov, K. S., et al., Science (2004)



Direct lattice

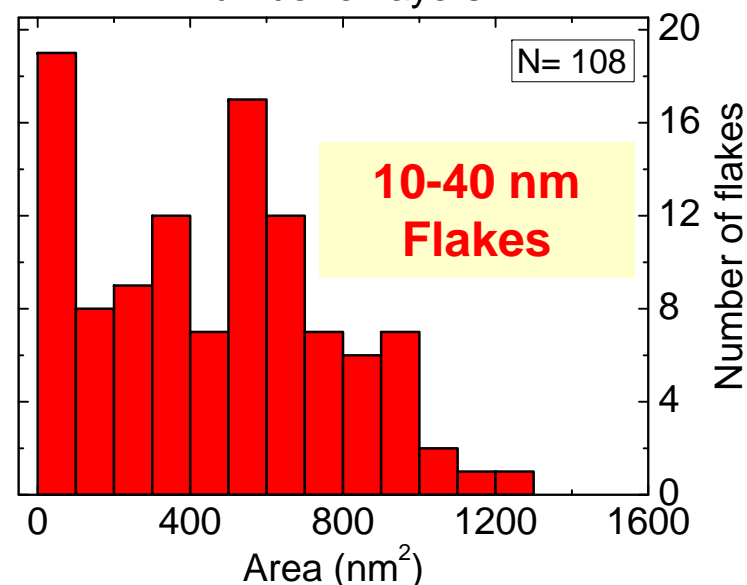
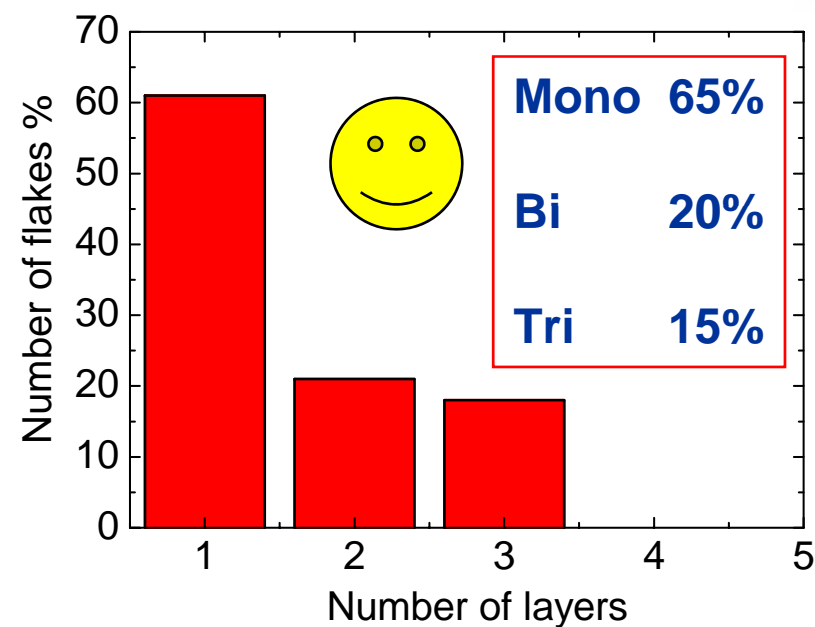
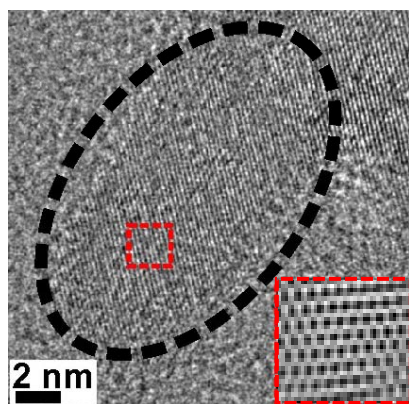
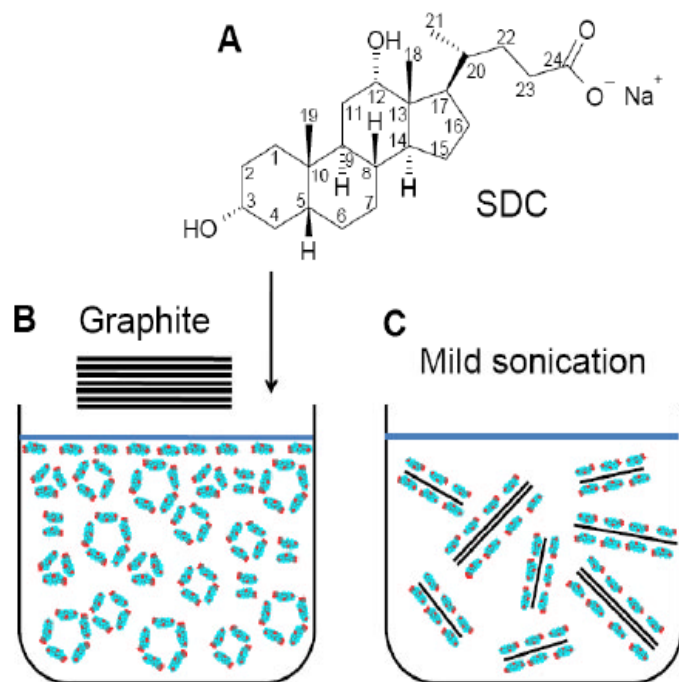


Brillouin zone



A.H. Castro-Neto et al., Rev. Mod. Phys. (2009)

Applications to Photonics: F.Bonaccorso et al., Nature Photon. (2010)



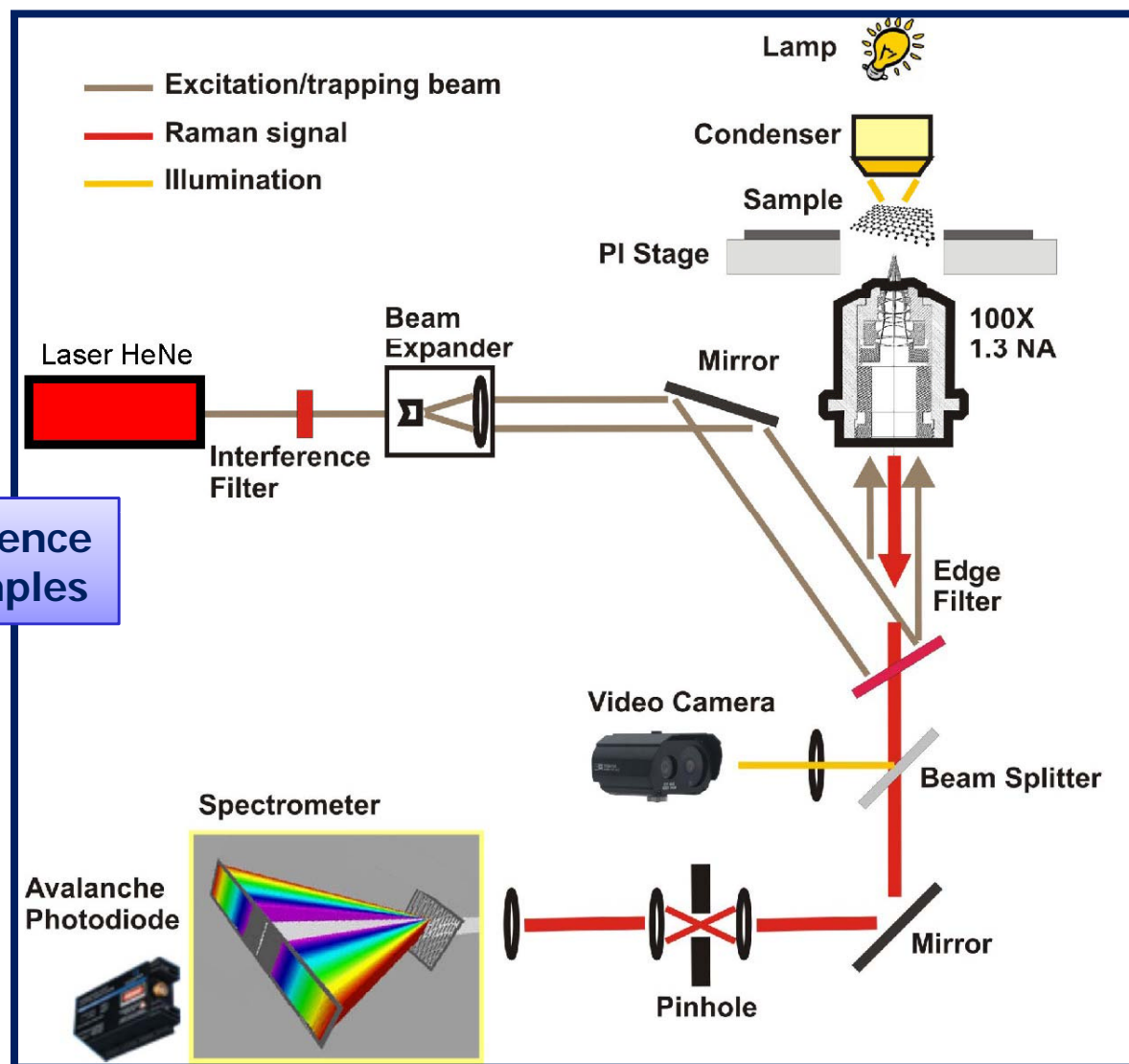
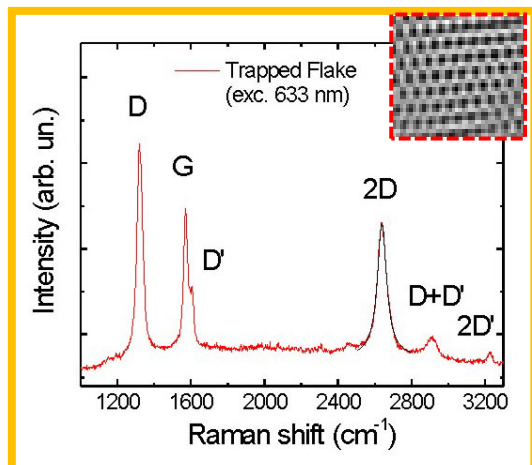
Y. Hernandez et al. Nature Nanotech. 3, 563 (2008)

O.M. Maragò et al. ACS Nano **4**, 7515 (2010)

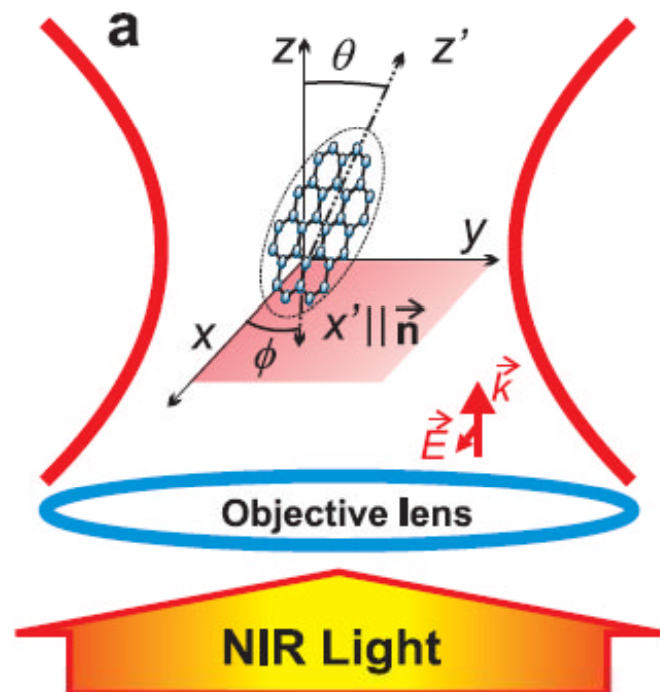
- HeNe 633nm, 10 mW
- Edge filter@633nm
- Jobin-Yvon Triax 190 spectrometer
- Avalanche photodiode, SPC (Perkin Elmer)

Raman & Photoluminescence inspection of trapped samples

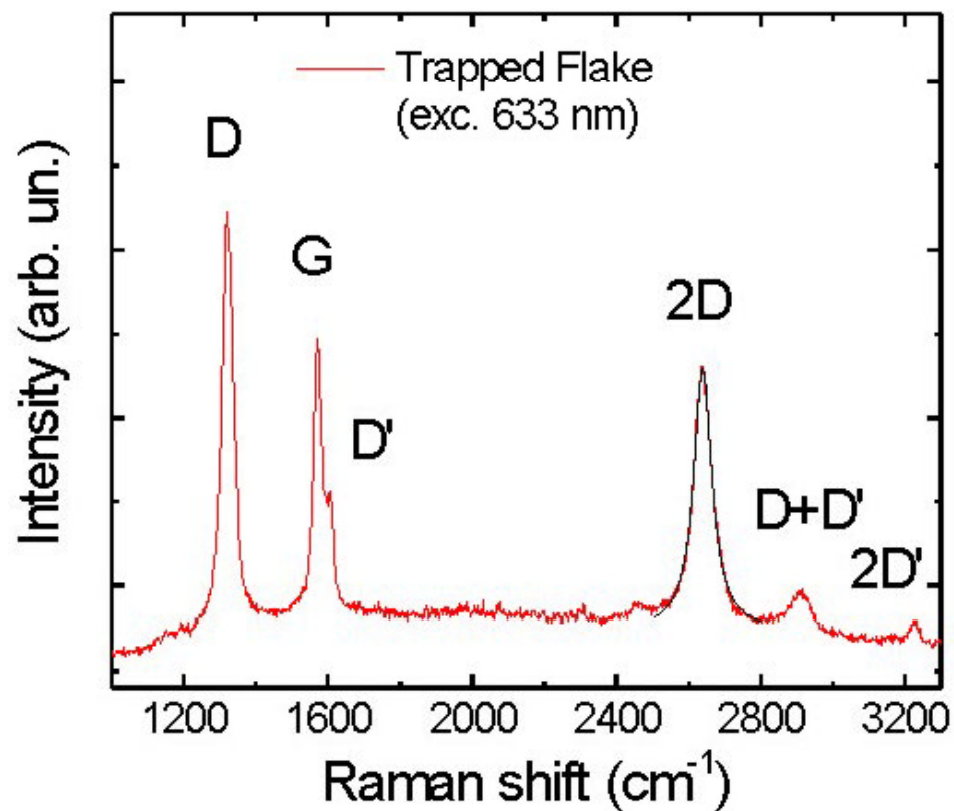
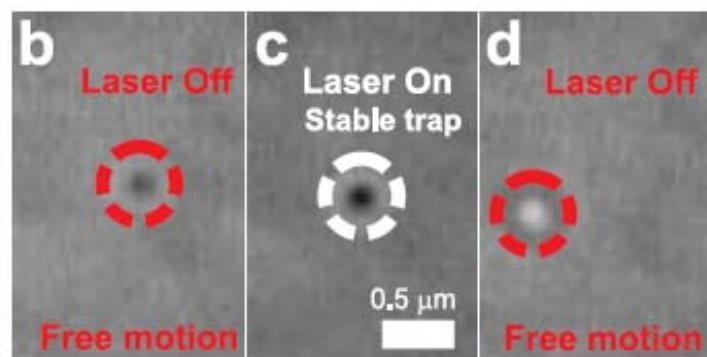
E.g., Inspection of **Graphene** flakes



Maragò, O.M., et al., *ACS Nano* **4**, 7515 (2010)



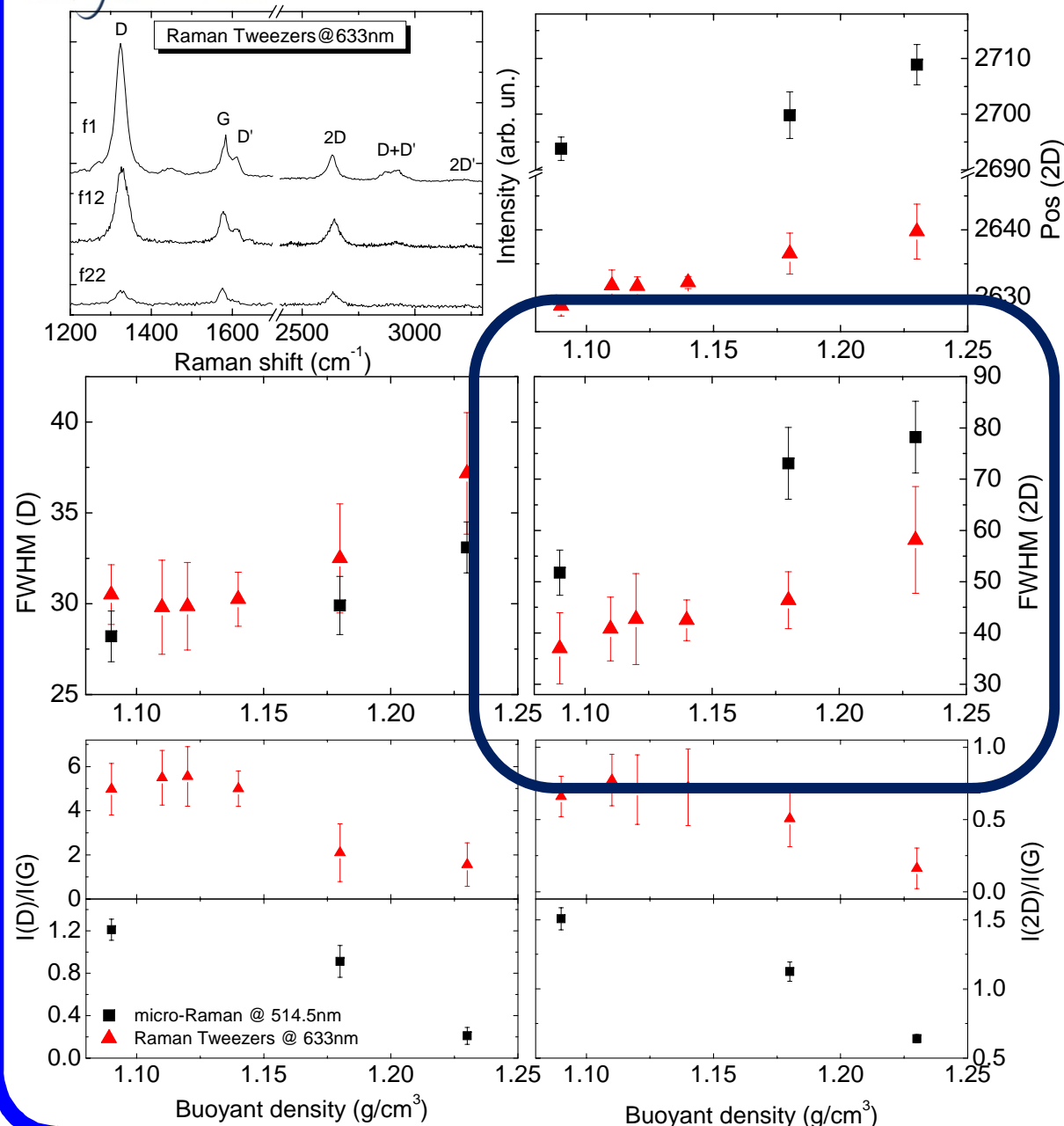
**Low power (2 mW) for stable OT
AND Raman @633nm**



Maragò, O.M., et al., ACS Nano (2010)

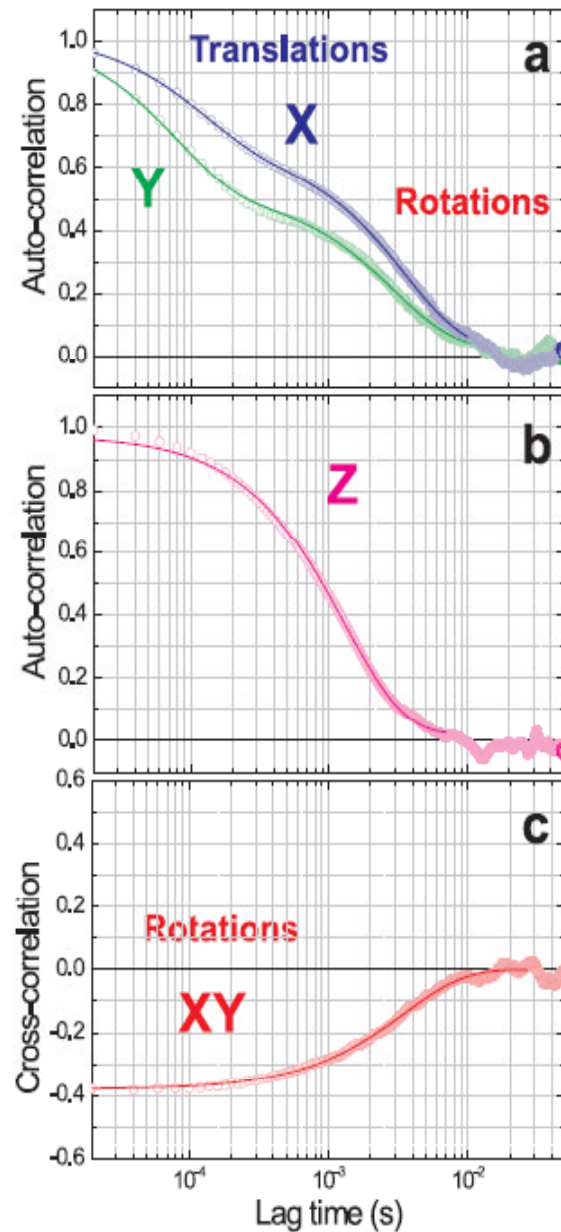


RT Spectroscopy on DGU Flakes



•We trap individual flakes and measure smaller FWHM than micro-Raman on a substrate

•Top fractions show up to 70% monolayer flakes consistent with TEM analysis



Hydrodynamics

$$\begin{aligned}\gamma_{\parallel} &= 8\eta D \\ \gamma_{\perp} &= \frac{16}{3}\eta D \\ \gamma^r &= \frac{4}{3}\eta D^3\end{aligned}$$

Langevin

$$\begin{aligned}\partial_t X(t) &= -\Gamma_{\perp} k_x X(t) + \xi_x(t) \\ \partial_t Y(t) &= -\Gamma_{\parallel} k_y Y(t) + \xi_y(t) \\ \partial_t Z(t) &= -\Gamma_{\perp} k_z Z(t) + \xi_z(t) \\ \partial_t \phi(t) &= -\Gamma^r k_{\phi} \phi(t) + \xi_{\phi}(t) \\ \partial_t \theta(t) &= -\Gamma^r k_{\theta} \theta(t) + \xi_{\theta}(t)\end{aligned}$$

QPD Signals and Correlations

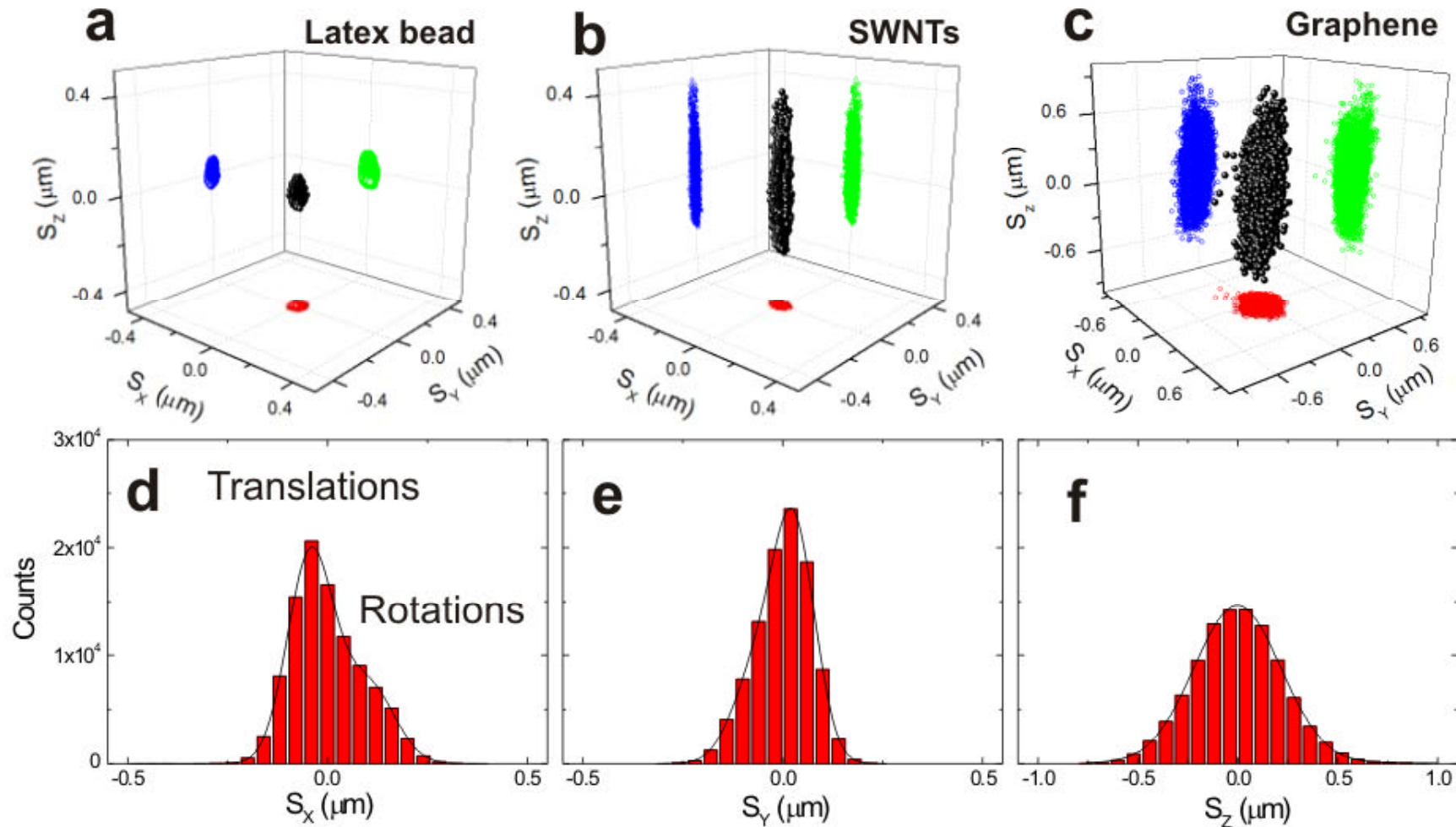
$$S_x \sim \beta_x (X - a\phi + b\theta); S_y \sim \beta_y (Y + c\phi); S_z \sim \beta_z Z$$

$$C_{xx} \approx \beta_x^2 [C_{XX} + A^2 C_{\phi\phi} + B^2 C_{\theta\theta}]$$

$$C_{yy} \approx \beta_y^2 [C_{YY} + C^2 C_{\phi\phi}]$$

$$C_{zz} \approx \beta_z^2 C_{ZZ}$$

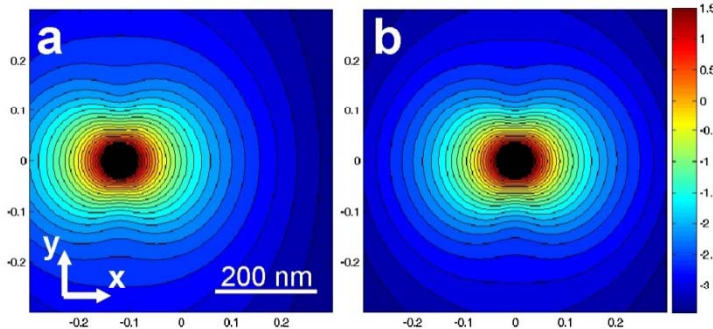
$$C_{xy} \approx -\beta_x \beta_y A C C_{\phi\phi}$$



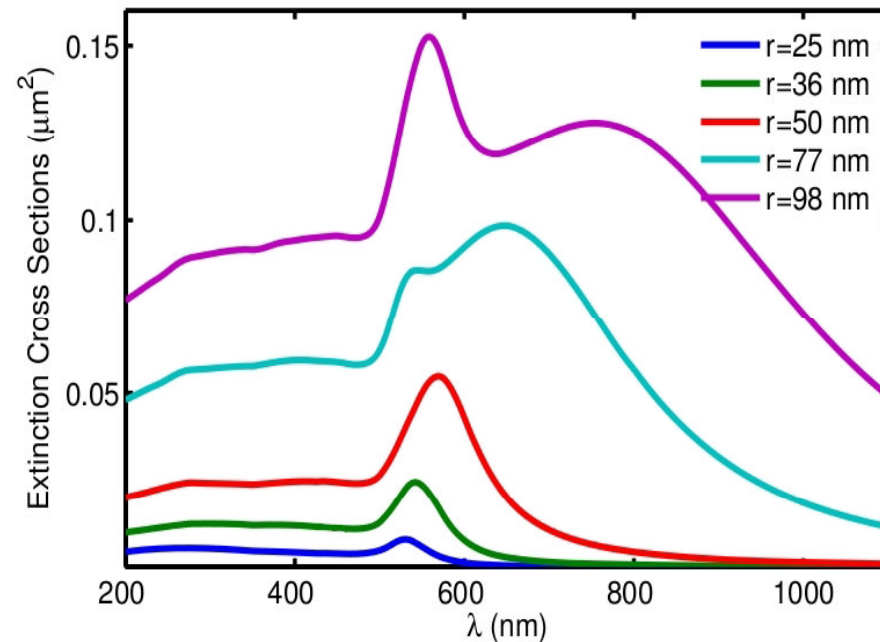
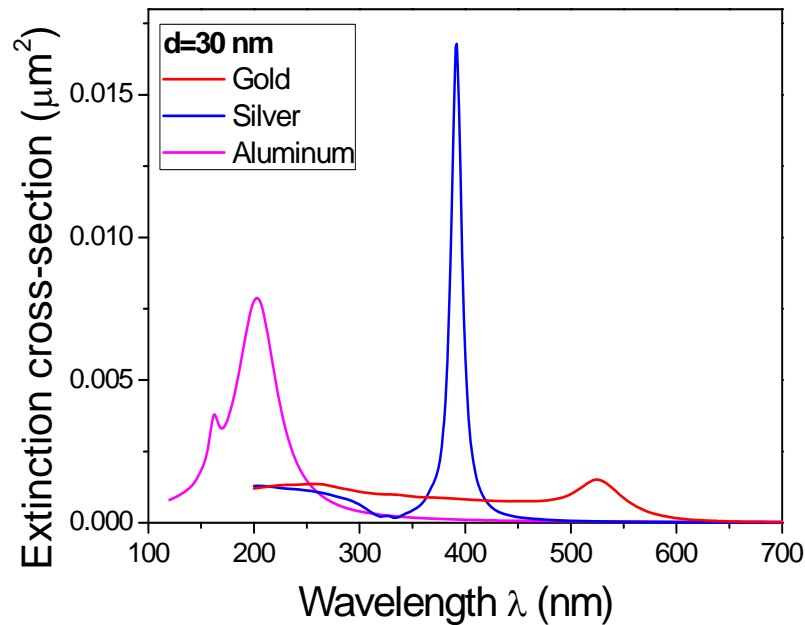
Angular fluctuations within **7 deg**
 Transverse fluctuations **50 nm**
 Axial fluctuations **200 nm**

Torque **6 fN nm/rad**
 Transverse Force **1.5 pN/ μ m**
 Axial Force **0.1 pN/ μ m**

Plasmon-enhanced Optical Trapping (1)



For **metal nanoparticles**, the presence of **plasmon resonances** leads to their optical trapping with a wavelength in the **red side** of the spectrum.



Saija R et al. Optics Express (2009)

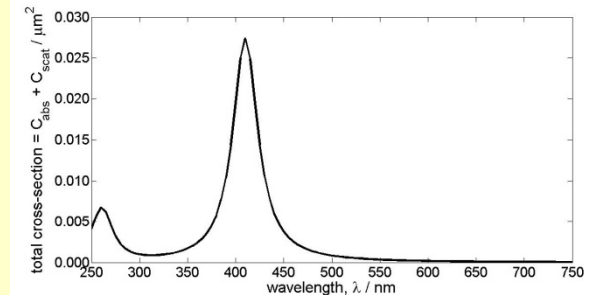
Plasmon-enhanced Optical Trapping (2)

Lorentz-Drude model for dielectric constant using tabulated fit parameters that agrees well with experimental data and exploit plasmon resonance to enhance optical forces

$$\varepsilon(\omega) = \varepsilon_{\infty} + \sum_{k=1}^K \frac{f_k \omega_p^2}{\omega_k^2 - \omega^2 + i\omega\Gamma_k}$$

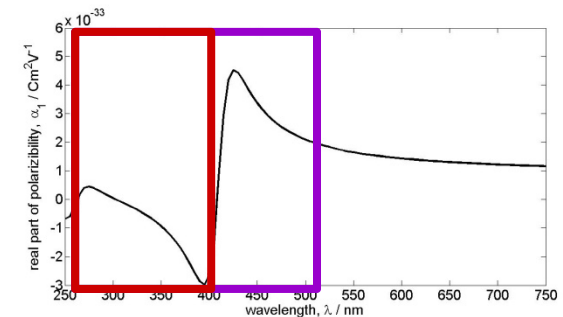
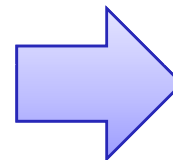
$$\alpha(\omega) = 4\pi\varepsilon_0 a^3 \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}$$

$$C_{abs} = \frac{k}{\varepsilon_0} \text{Im}\{\alpha(\omega)\}; \quad C_{scat} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha(\omega)|^2$$

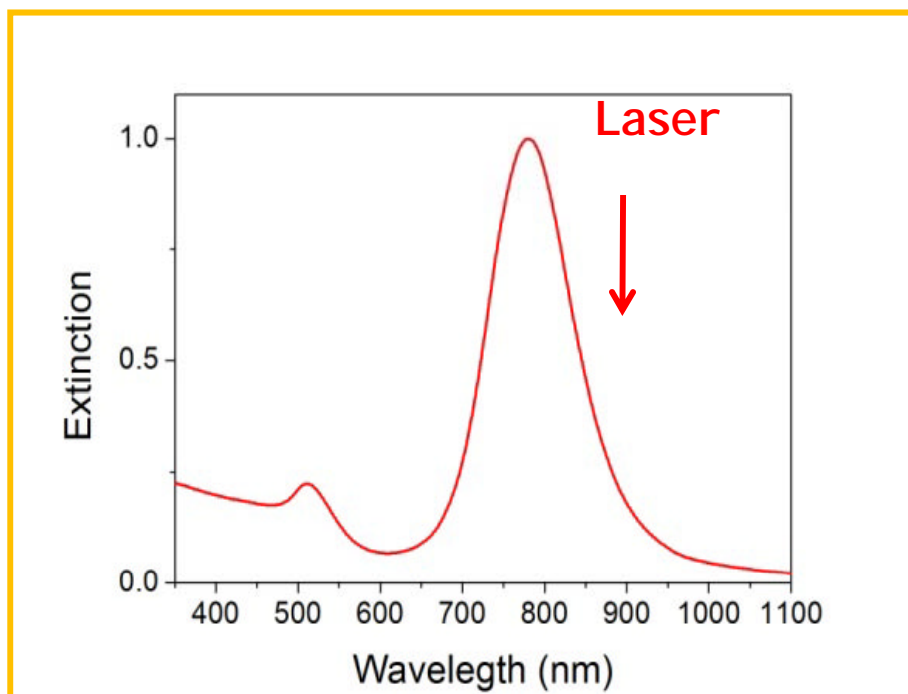


$$F_{scat.}(r) = \frac{k^4 \alpha^2}{6\pi c n^3 \varepsilon_0^2} I(r)$$

$$\langle F_{grad} \rangle = \frac{1}{2} \text{Re}\{\alpha(\omega)\} \nabla \langle |E|^2 \rangle$$

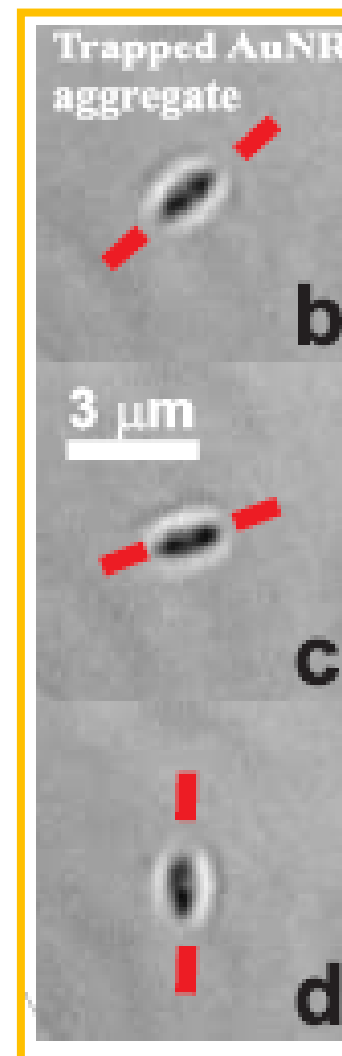


Polarization Orientation of Nanorods (Shape Matters!)

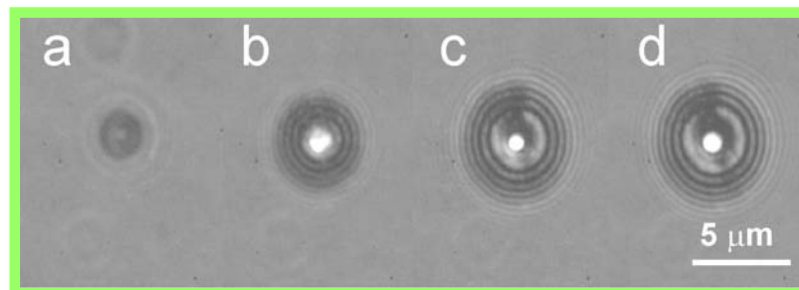
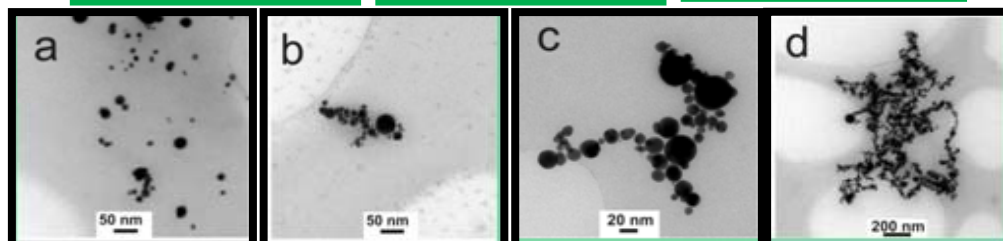
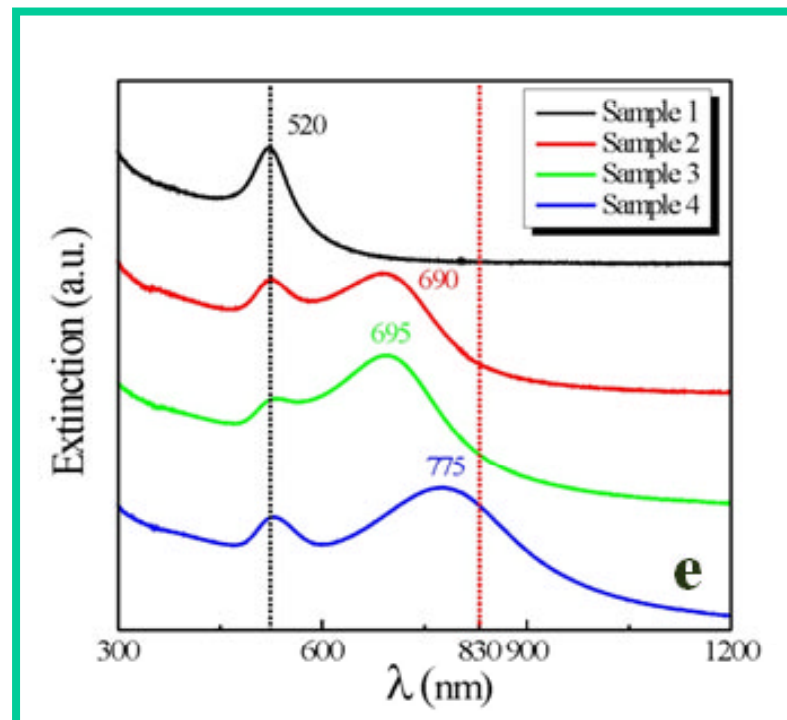
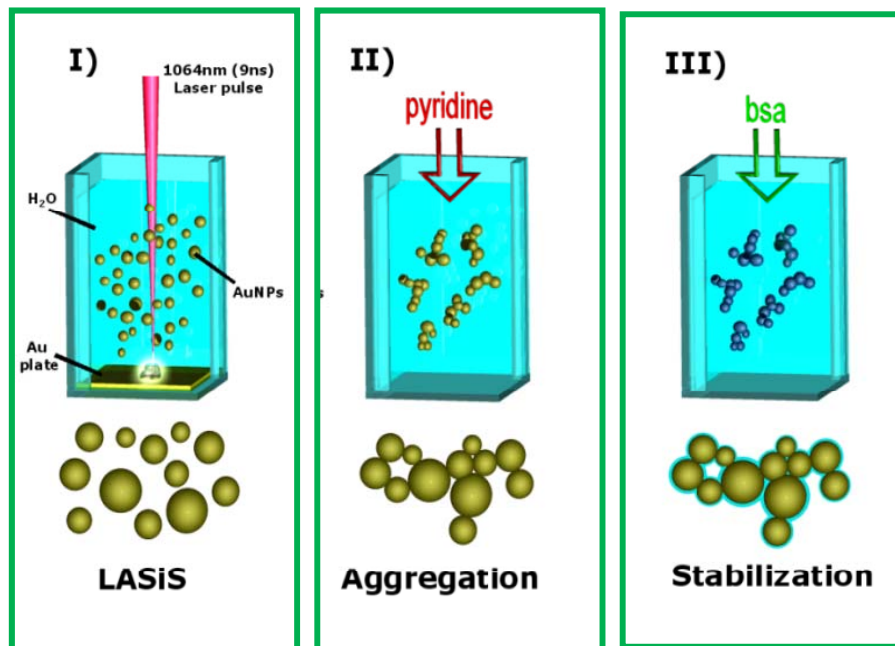


Gold Nanorods align with polarization in the trap and they can be easily rotated.

Jones et al., *ACS Nano* (2009) 3, 3077–3084



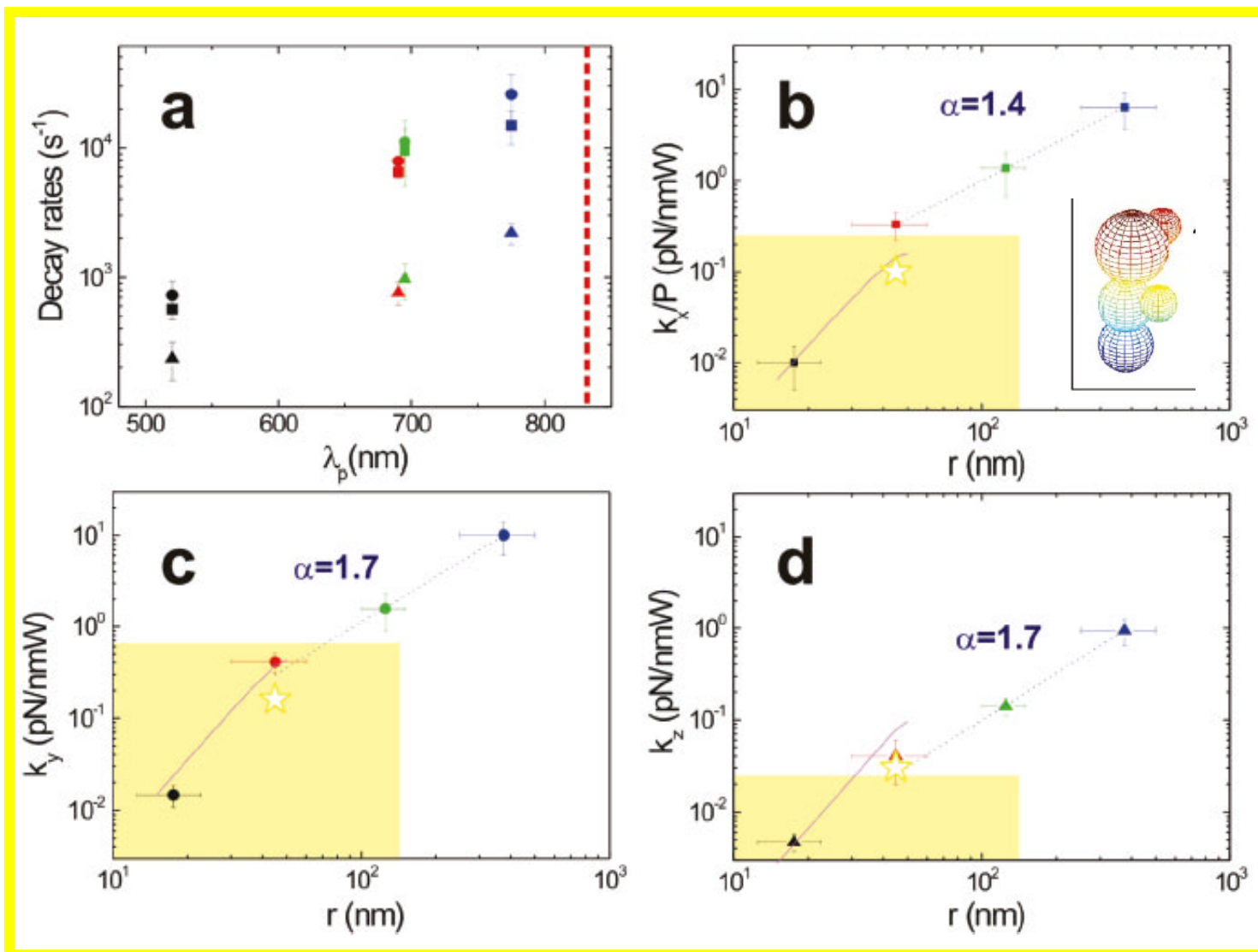
LASiS



Messina et al., *ACS Nano* 5, 905 (2011)

Also used for **Magneto-Plasmonic** (Au-Fe) Nanostructures!

Messina et al., ACS Nano 5, 905 (2011)

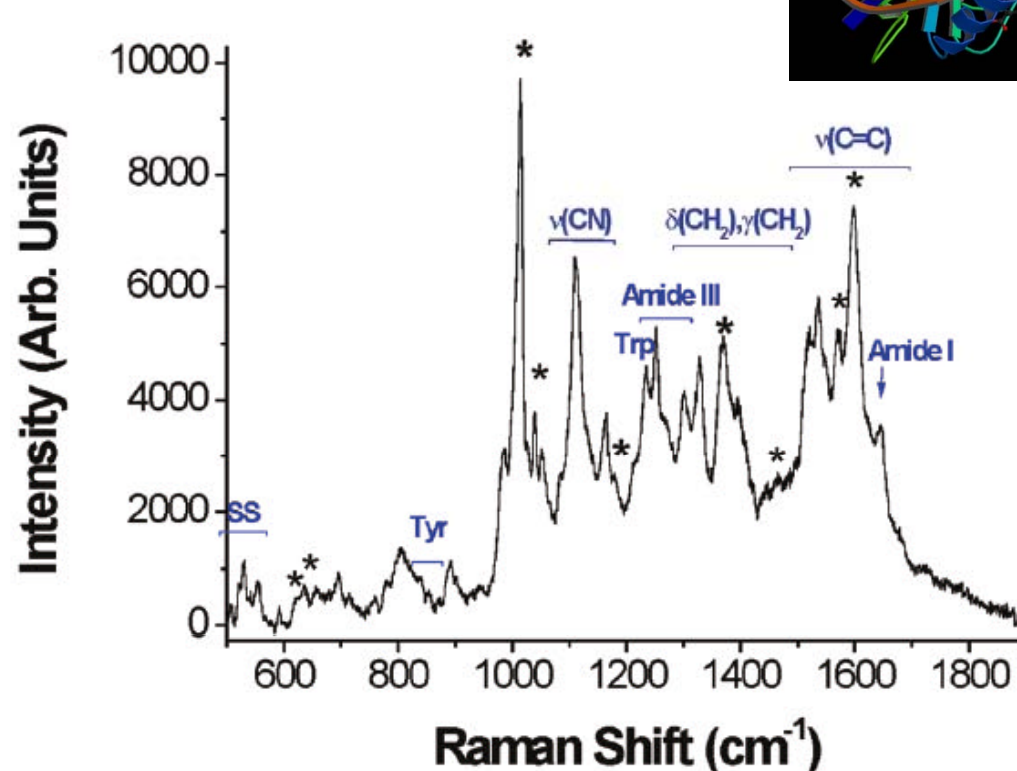
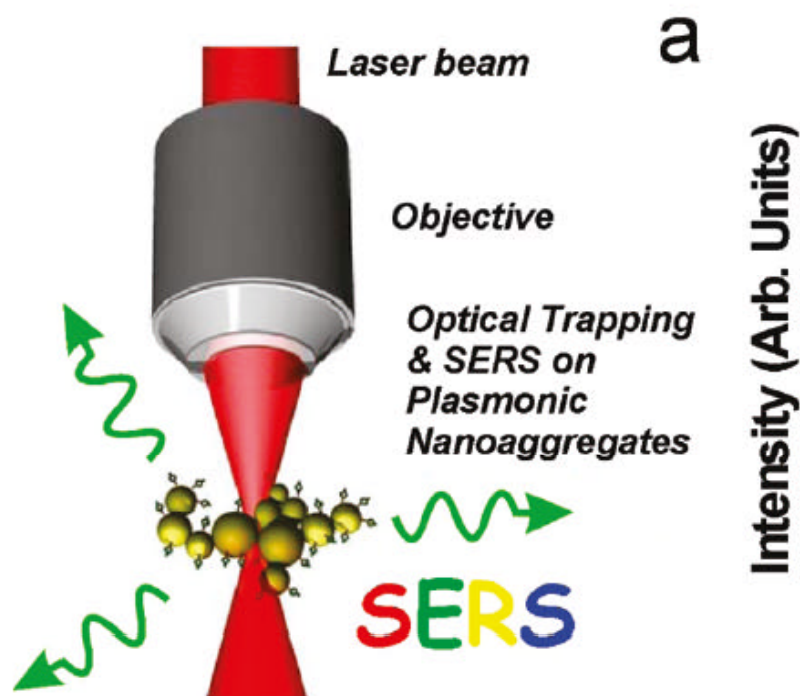
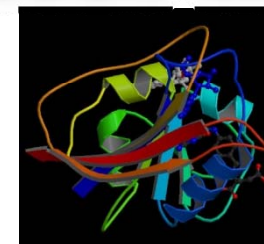


Force on a sphere has volumetric scaling, while for an **Aggregate** **Scaling** reflects its **Fractal** structure

Surface-Enhanced Raman Tweezers

BOVINE SERUM
ALBUMIN (BSA)

Use the SAME light to trap and excite SERS
Trapping wavelength 785nm > 695nm MNP Aggregate SPR



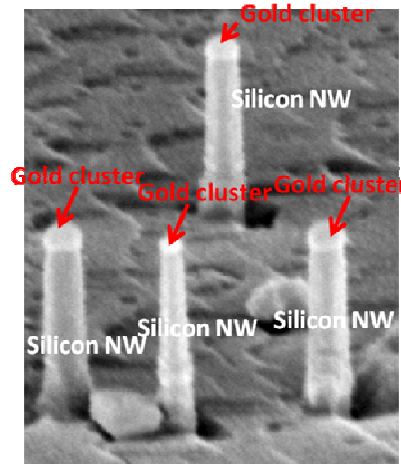
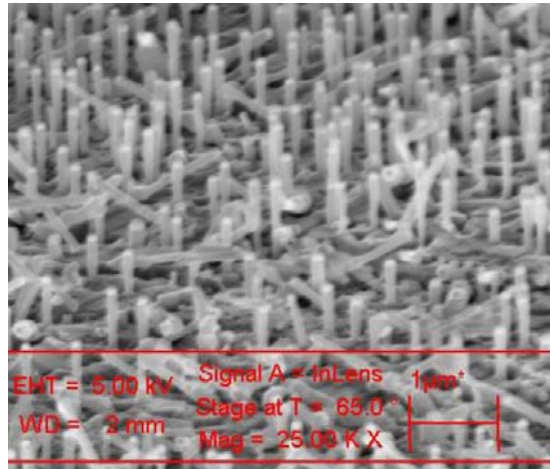
Messina et al., *J Phys Chem C* 115, 5115 (2011)



Active Plasmonic Nanoswimmers



Collaboration with F. Priolo (Catania) & G. Volpe (Bilkent)



Si Nanowires with a Gold NP

Length=800 nm

Width= 100 nm

Interesting for optical trapping,
probing, spectroscopy, ...

Green Laser off
Sad nanoswimmer!



Green Laser on
Happy nanoswimmer!

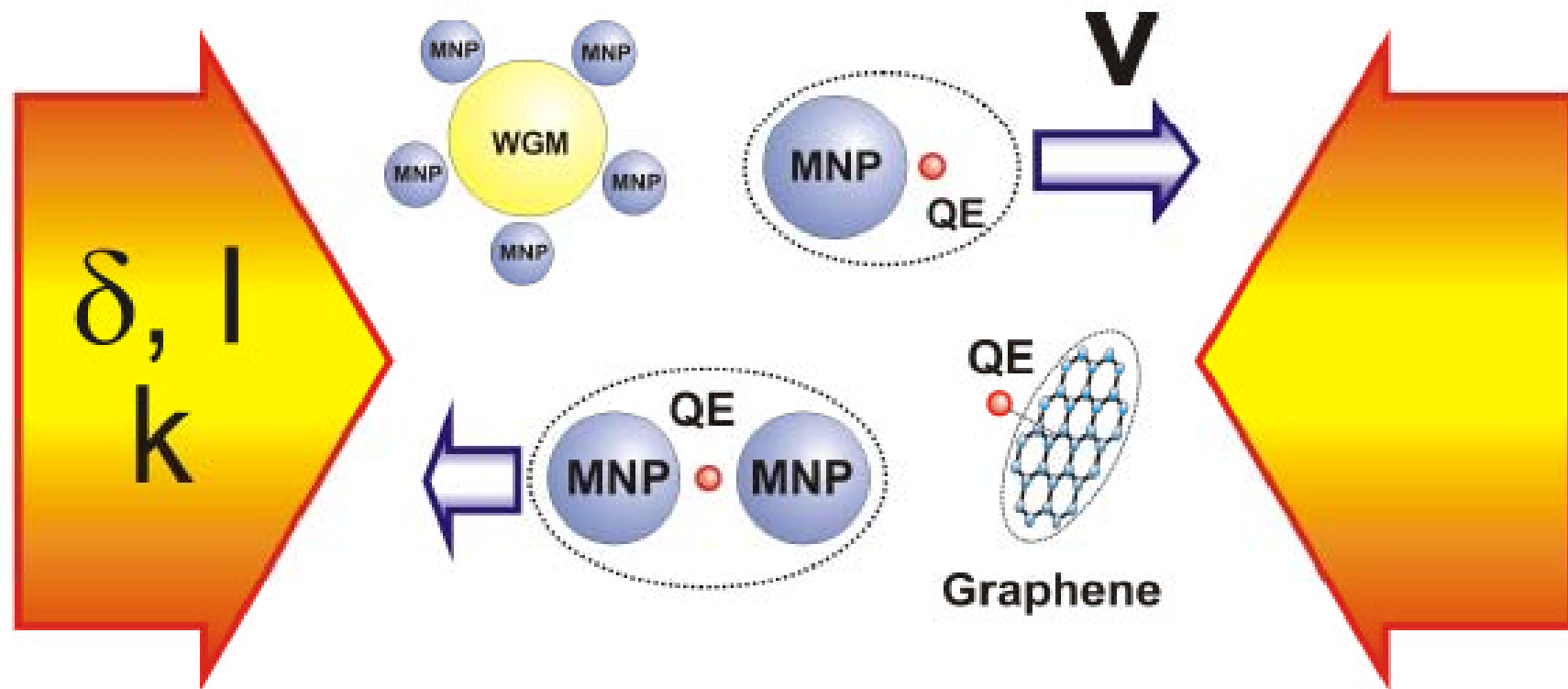


**Tunable & Directional
Brownian Motion**

Self-Diffusiophoresis in a
critical mixture

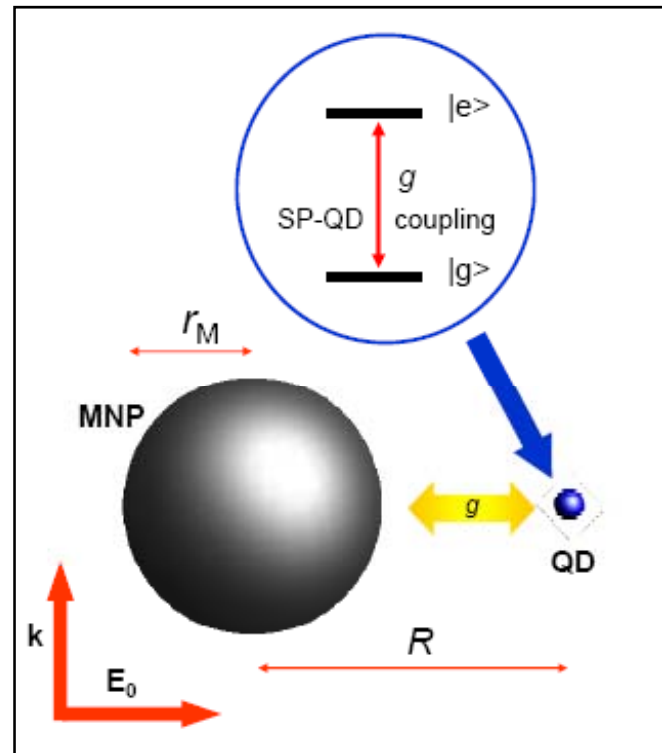


Can we apply Laser Cooling to Nanostructures?



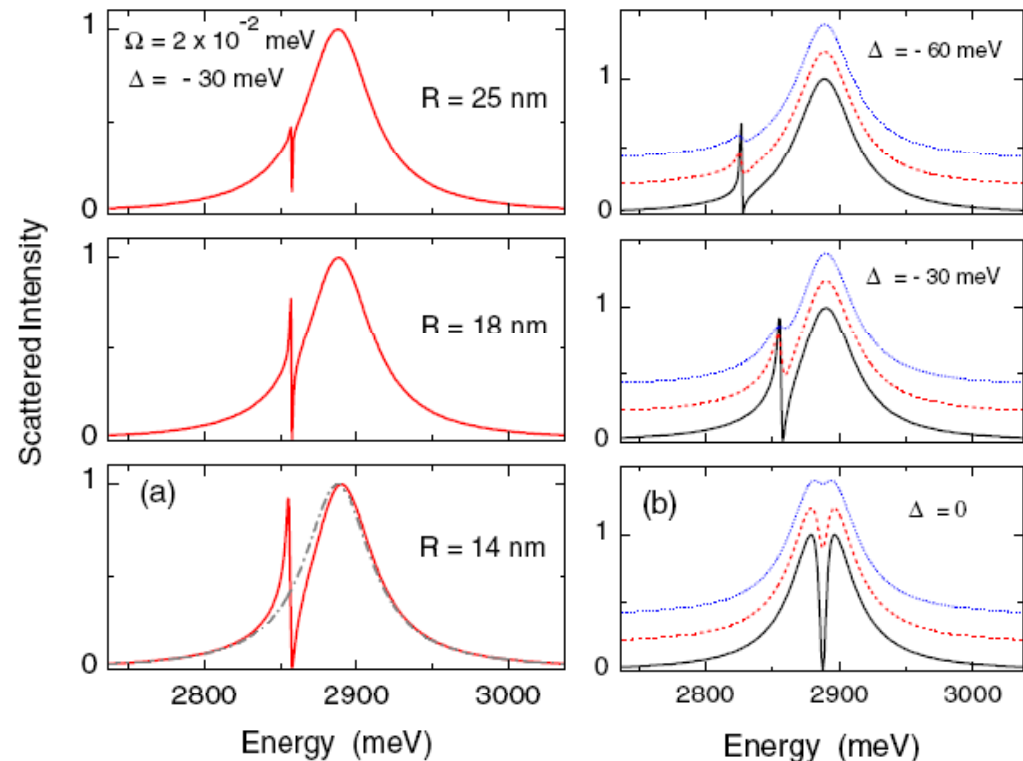
Hybridization of Nanostructures plays a crucial role in getting Quantum resonances that can help the Laser Cooling.

A. Ridolfo et al., PRL (2010);
S. Savasta et al., ACS Nano (2010)



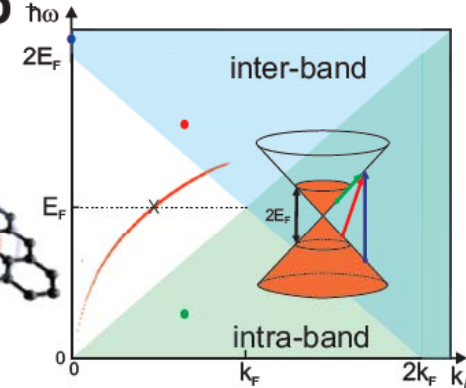
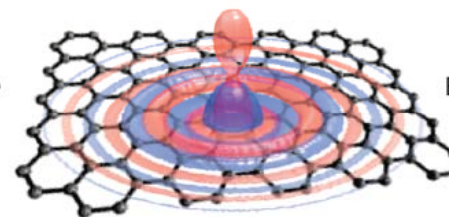
The MNP-QD molecule is a
saturable scatterer

Koppens et al., *Nano Lett.*, **2011**, 11, 3370–3377



a

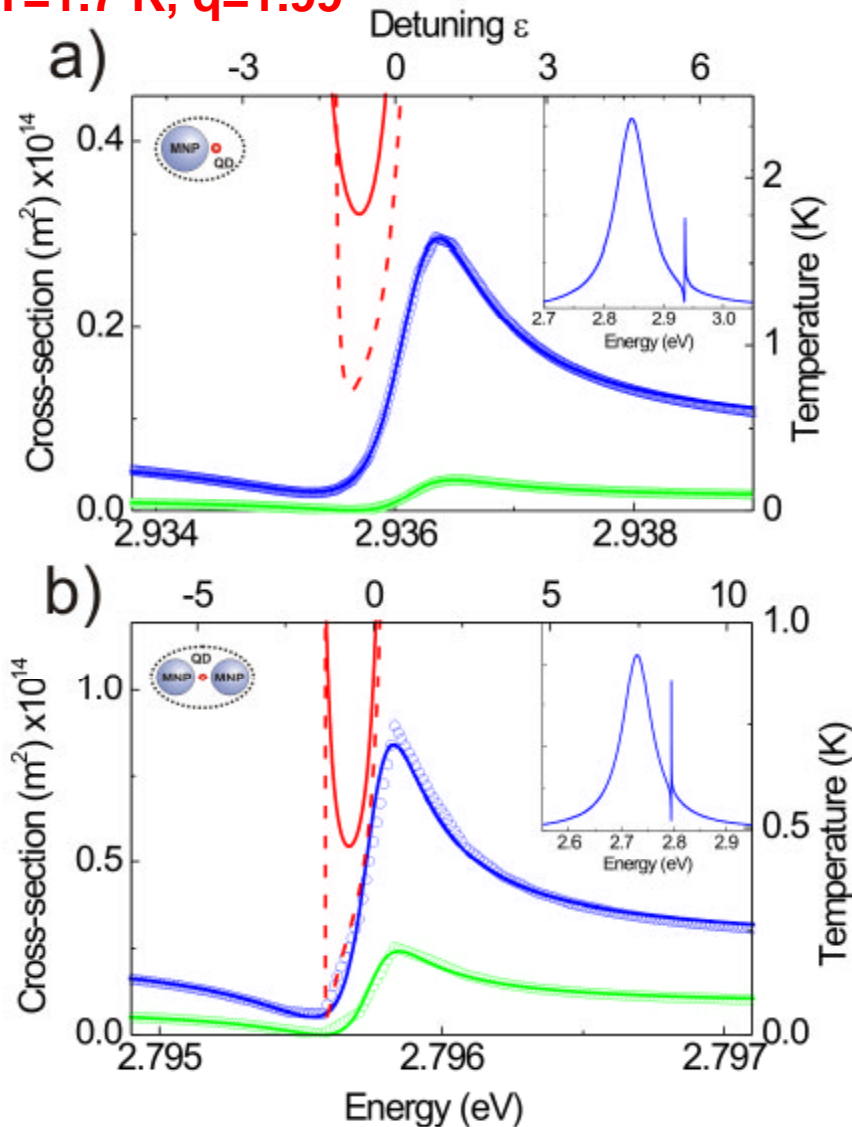
b



Sub-Doppler Temperature



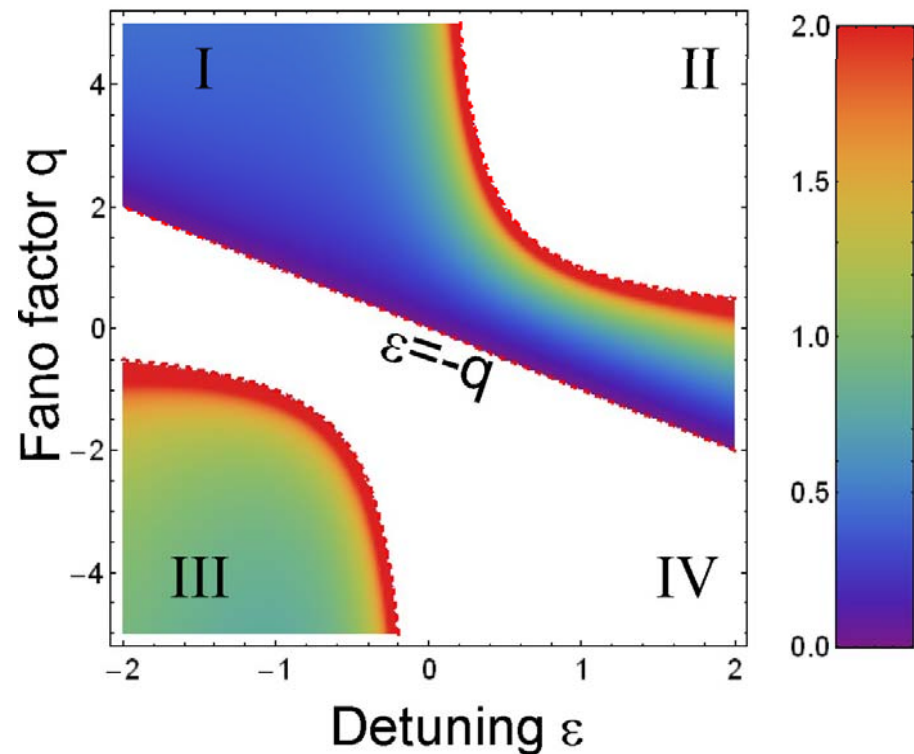
T=1.7 K, q=1.99



T=450 mK, q=1.71

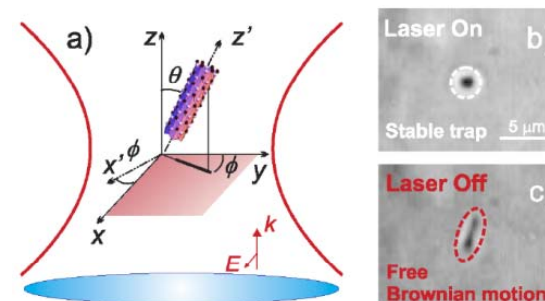
Temperature from the diffusion process in momentum space. Balance between cooling and scattering processes.

$$\frac{T_F}{T_D} = \frac{(q + \epsilon)(\epsilon^2 + 1)}{2(1 - \epsilon q)}$$



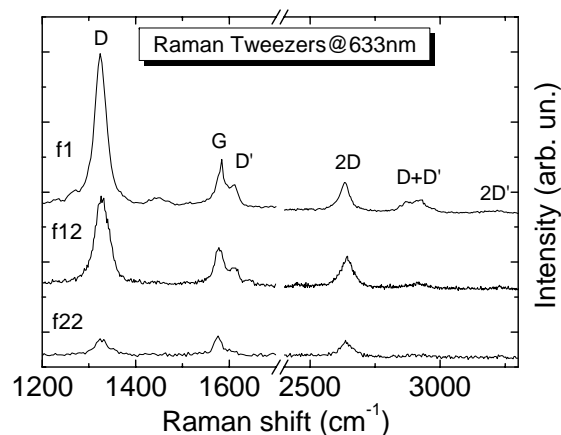
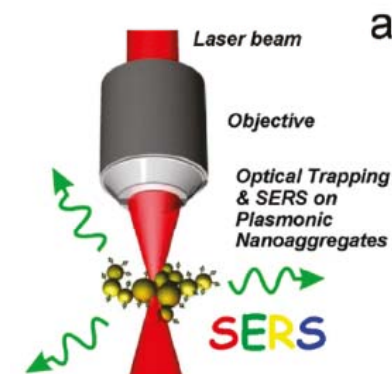
Optical Trapping of Linear Nanostructures (Nanotubes & Nanowires)

- Brownian Motion – Role of 1D Geometry
- Force Sensing with Nanotubes (Nanotube-PFM)
- Raman & PL Tweezers (Individual bundle spectroscopy)
- Size-Scaling in OT of Linear Nanostructures



Plasmon-enhanced Optical Trapping of MNPs

- Measure of Optical Forces & Rotations
- Force Calculations and Scaling Laws
- SERS with Trapped Nanoaggregates

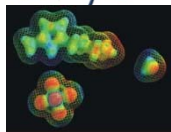


Optical Trapping of Graphene

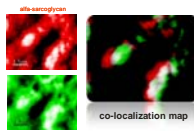
- Brownian Motion – Role of 2D Geometry
- Light forces on Graphene flakes
- Raman Tweezers (Individual flake spectroscopy)



Acknowledgements



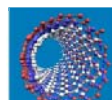
NanoSoftLab



P. G. Gucciardi (SNOM/SERS/TERS/NANOAntenna)

E. Messina (Post-doc)

C. D'Andrea (PhD), **A. Foti** (Diploma)



B. Fazio (Raman Spectroscopy, SERS)

M.G. Donato (Carbon nanostructures/Optical Tweezers)

M. A. Iatì (E.M. Scattering Theory)

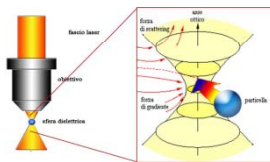


A. Cacciola (PhD, Theory)

A. Irrera (Nanostructured Semiconductors)

O. M. Maragò (Optical Trapping)

M. Monaca & R. Sayed (PhD)



S. Vasi & R. Stornante (Diploma)

P. Princi (Bio-Informatics)

R. Saija, P. Denti, F. Borghese (UniMessina, ELS Theory)

S. Savasta (UniMessina, Quantum Optics Theory)

OT Collaborations

F. Bonaccorso

A.C. Ferrari



P.H. Jones

V. Amendola



F. Priolo

G. Compagnini

G. Volpe



A. Camposeo



THE ROYAL SOCIETY





Thank You!!!