# Ion interactions with carbon nano-structures

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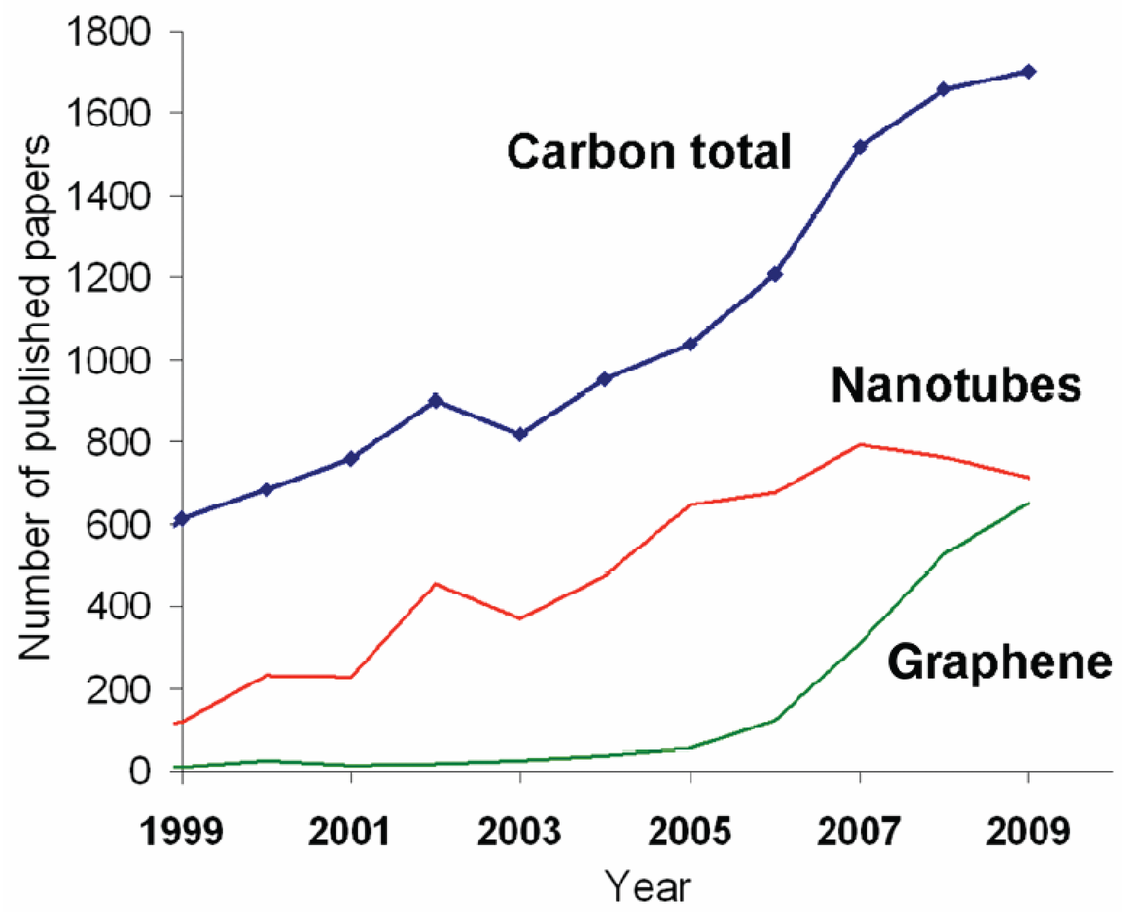
*Support:* NSERC & PREA

# Outline

- ❑ Introduction
- ❑ Interactions of fast ions with CNTs
  - Plasmon excitations: oblique incidence
  - Ion channeling: rainbow effect
- ❑ Interactions of slow ions with graphene
  - Nonlinear static screening
  - Dynamic screening: wake, stopping, image
  - Plasmon hybridization with substrate phonons
- ❑ Outlook

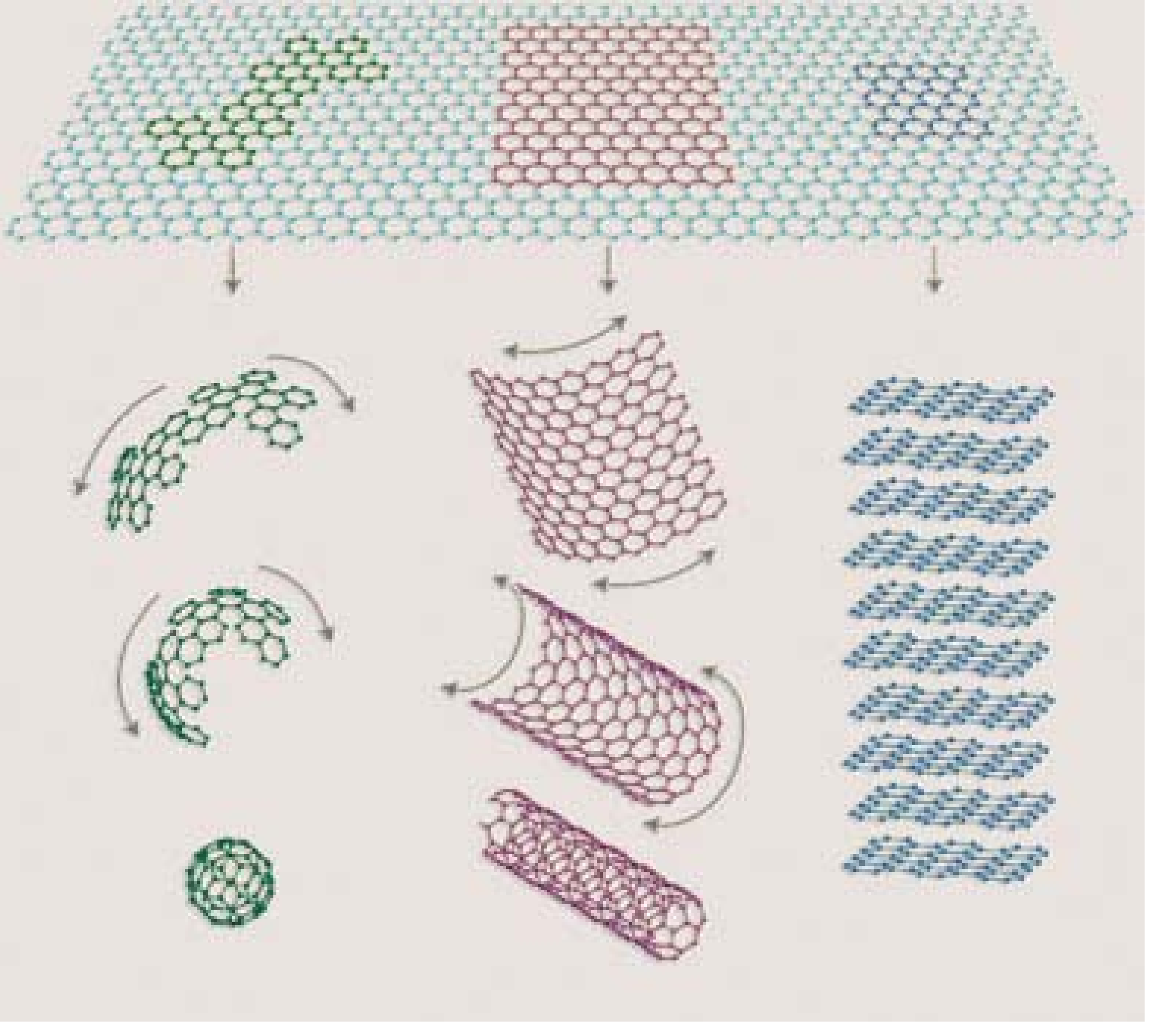
# Number of publications on carbon nanostructures

M.S. Dresselhaus, *ACS Nano* 4 (2010) 4344



# Graphene as building block of carbon nanostructures

**graphene**



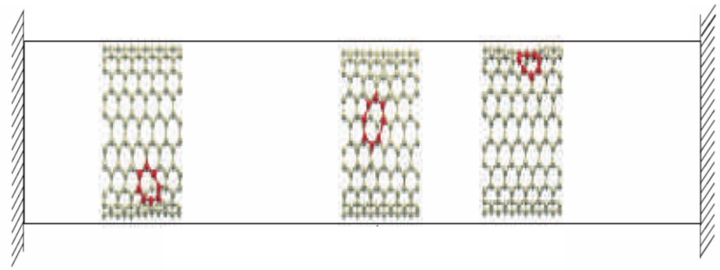
**Fullerene, $C_{60}$** **nanotube, CNT** **graphite, HOPG**

# Why study carbon nanostructures ?

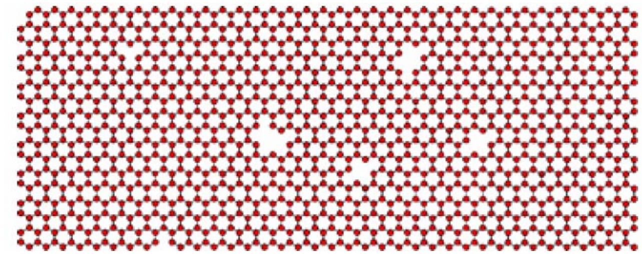
- Physical properties:
  - Electrical, mechanical, thermal
  - Dependent on: molecular structure, dielectric environment, local modification
- Applications:
  - Nanoelectronic devices
  - Biochemical sensors
  - New composite materials
  - Ion storage (H, Li)
  - Nanoelectromechanical systems (NEMS)

# Atomic-scale defects by ion irradiation (regime of nuclear stopping) *Krasheninnikov et al*.

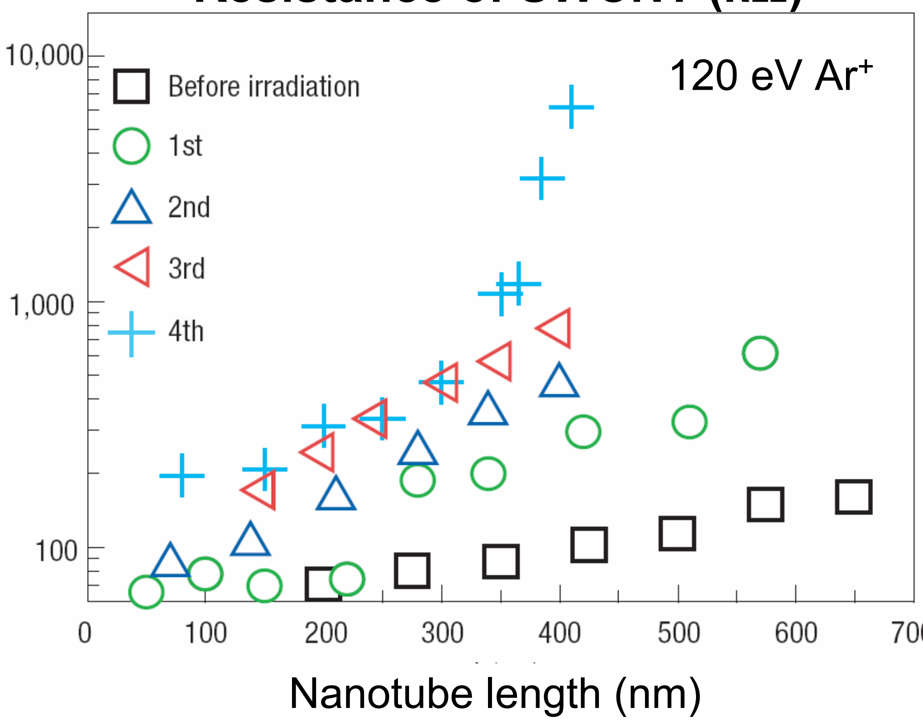
C. Gomez-Navarro *et al., Nature Mat.* (2005)



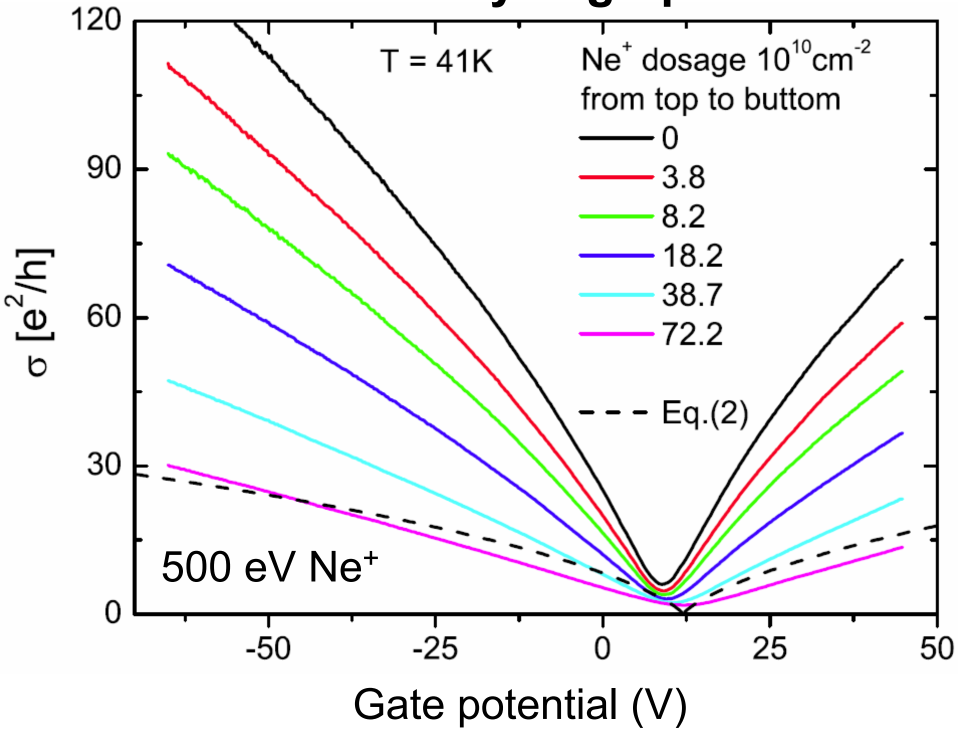
J.H. Chen *et al., Phys. Rev. Lett.* (2009)



**Resistance of SWCNT (kΩ)**




**Conductivity in graphene**



# Electronic response to external charged particles (regime of electronic stopping for moving particles)

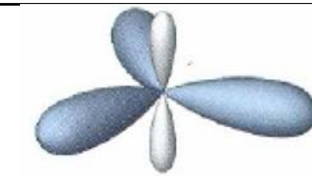
## ❑ Electrons

- EELS in STEM: plasmon excitations of σ and π electrons in CNTs & graphene
- HREELS: plasmon excitations of π electrons in graphene
- image potential states: CNTs & graphene

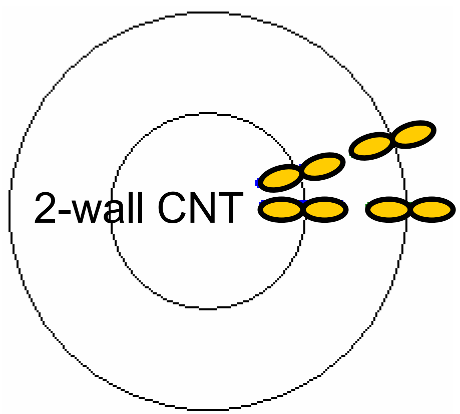
## ❑ Ions

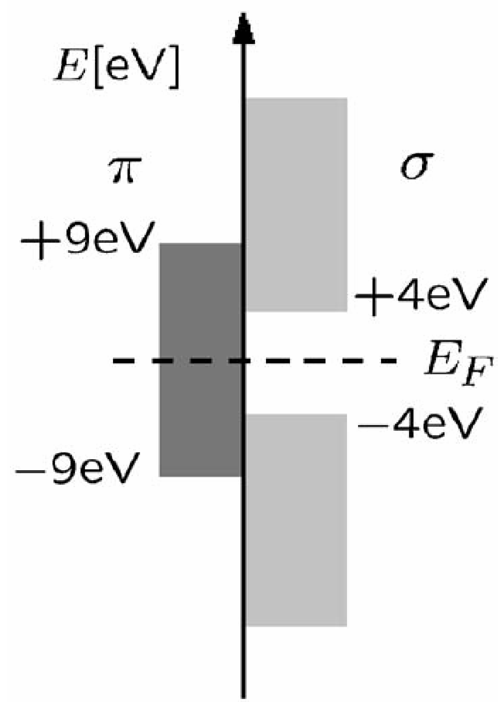
- ion channeling in CNTs
- grazing scattering of ions on graphene
- friction forces on slowly moving ions
- static screening of charged impurities

# Electronic structure: schematic

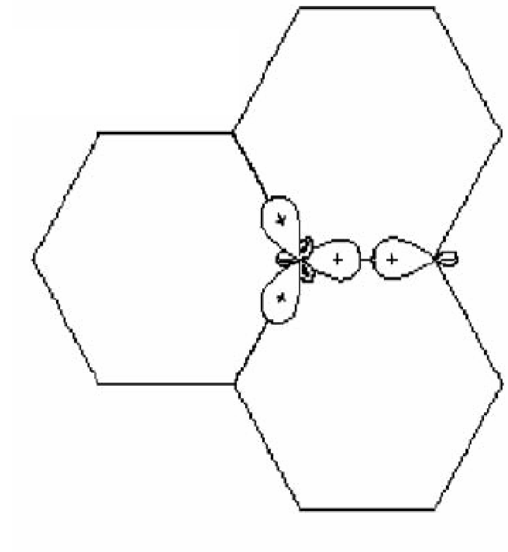


**π orbitals**

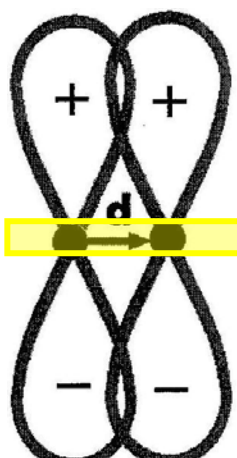


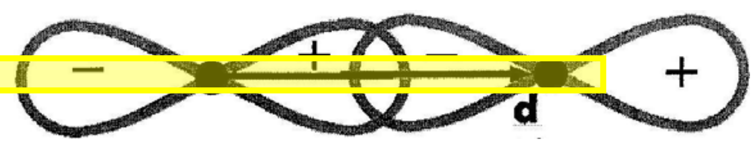

**σ orbitals**




dangling out of the layer




inside the layer



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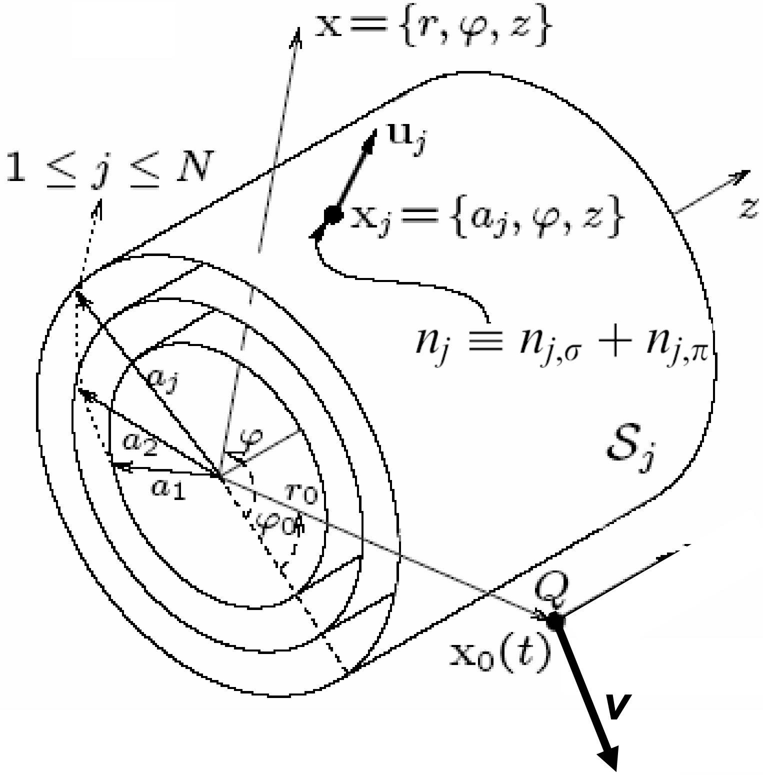
# Two-fluid, two-dimensional hydrodynamic model

D.J. Mowbray *et al., Phys. Rev.* B 70 (2004) 195418




$$\frac{\partial n_{j,\lambda}(\mathbf{x}_j,t)}{\partial t} + n_\lambda^0 \nabla_j \cdot \mathbf{u}_{j,\lambda}(\mathbf{x}_j,t) = 0$$

$$\frac{\partial \mathbf{u}_{j,\lambda}(\mathbf{x}_j,t)}{\partial t} = \nabla_j \Phi(\mathbf{x},t)|_{r=a_j} - \frac{\alpha_\lambda}{n_\lambda^0}\nabla_j n_{j,\lambda}(\mathbf{x}_j,t) + \frac{\beta}{n_\lambda^0}\nabla_j[\nabla_j^2\, n_{j,\lambda}(\mathbf{x}_j,t)] - \gamma_\lambda \mathbf{u}_{j,\lambda}(\mathbf{x}_j,t)$$

$$\Phi = \Phi_{\text{ext}} + \Phi_{\text{ind}}$$

$$\widetilde{\Phi}_{\text{ind}}(r,m,k,\omega) = -\sum_{j=1}^{N} g(r,a_j;m,k)\, a_j\, \widetilde{n}_j(m,k,\omega)$$

$$g(r,r';m,k) \equiv 4\pi I_m(|k|r_<)K_m(|k|r_>)$$

Stopping power

$$S = Q\frac{\partial \Phi_{ind}}{\partial z}\Big|_{\mathbf{x}=\mathbf{x}_0(t)}$$

Self-energy (image potential)

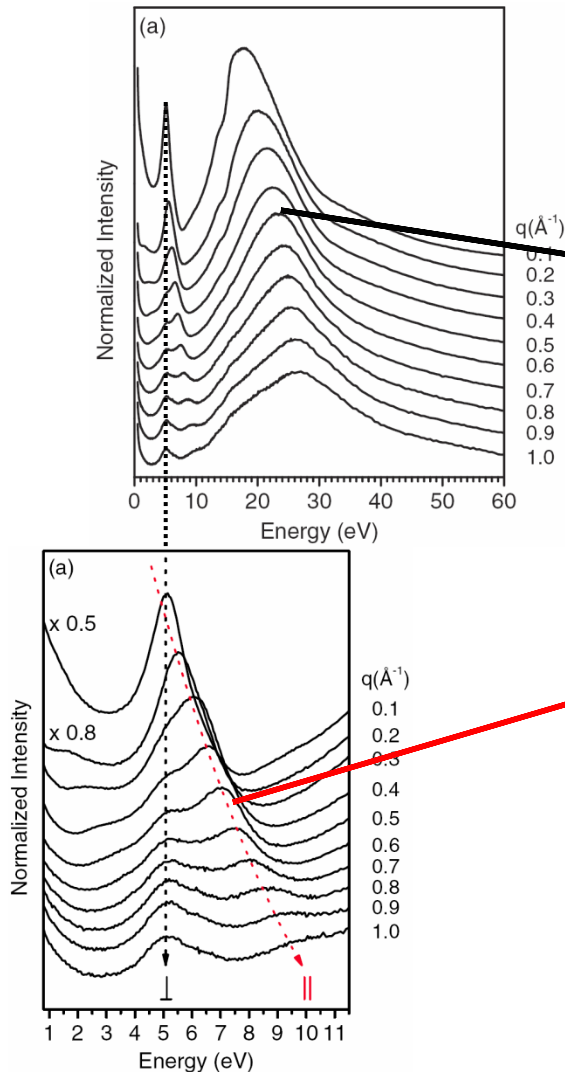
$$E_s = \frac{Q}{2}\Phi_{ind}\Big|_{\mathbf{x}=\mathbf{x}_0(t)}$$

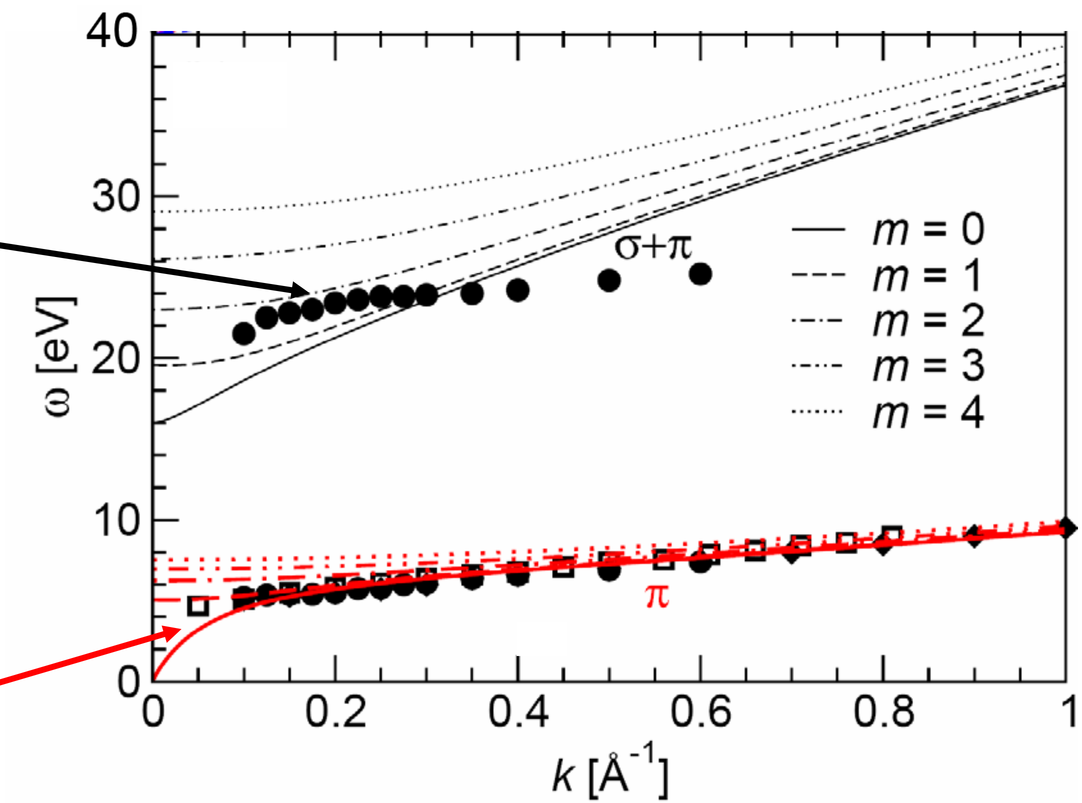
} For parallel trajectory

# Plasmon spectra: σ and π electrons on SWNT

EELS experiment: Kramberger *et al.*, *Phys. Rev. Lett.* 100 (2008) 196803

Plasmon dispersion curves: Mowbray *et al.*, *Phys. Rev.* B 82 (2010) 035405



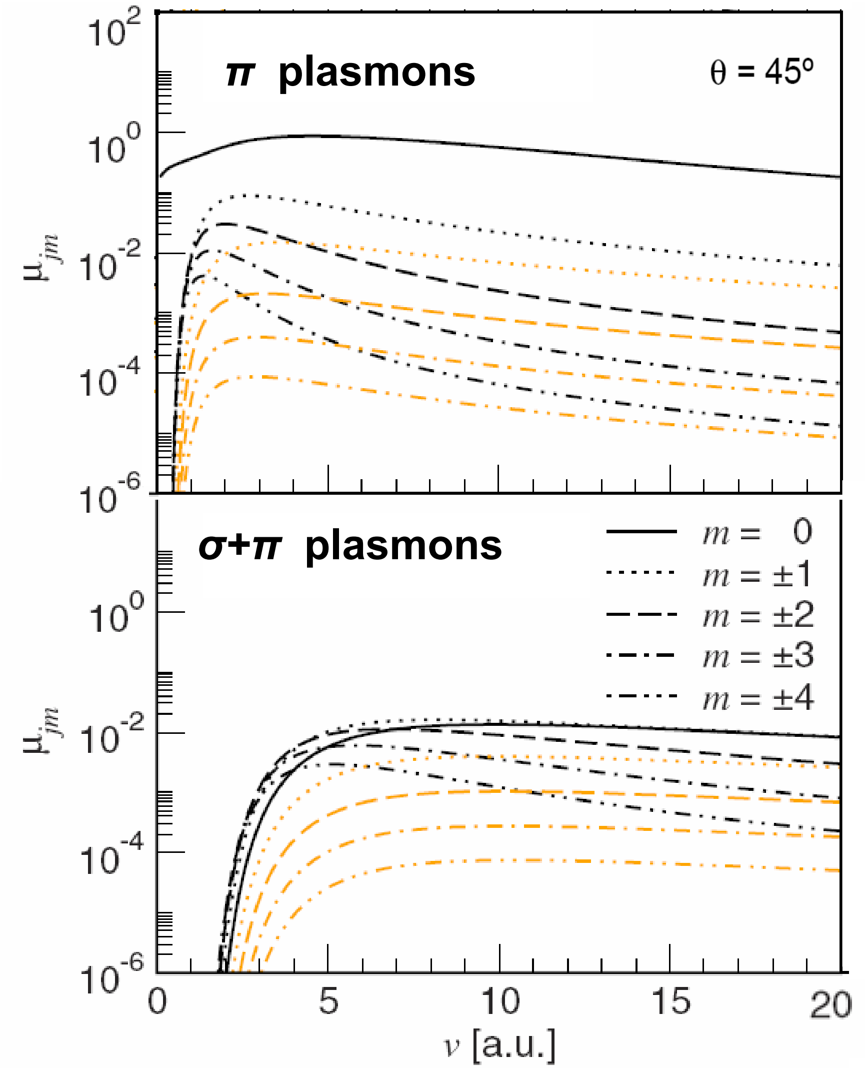




Thomas-Fermi-Dirac hydrodynamic model with restoring force for σ fluid

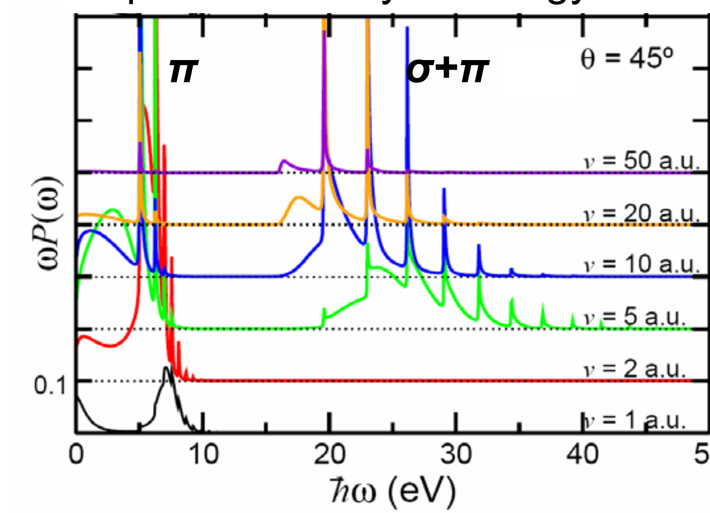
# Energy loss due to **oblique** incidence with angle θ

Mowbray *et al.*, *Phys. Rev.* B 82 (2010) 035405

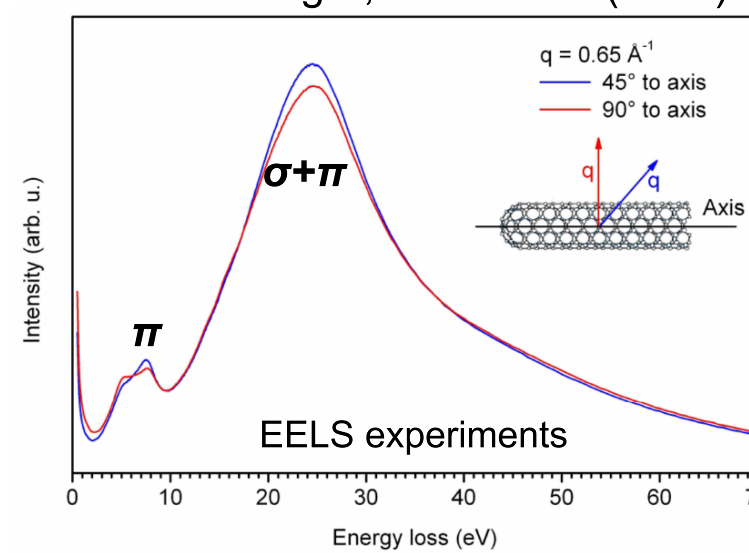
Average number of excited plasmons




Spectral density of energy loss



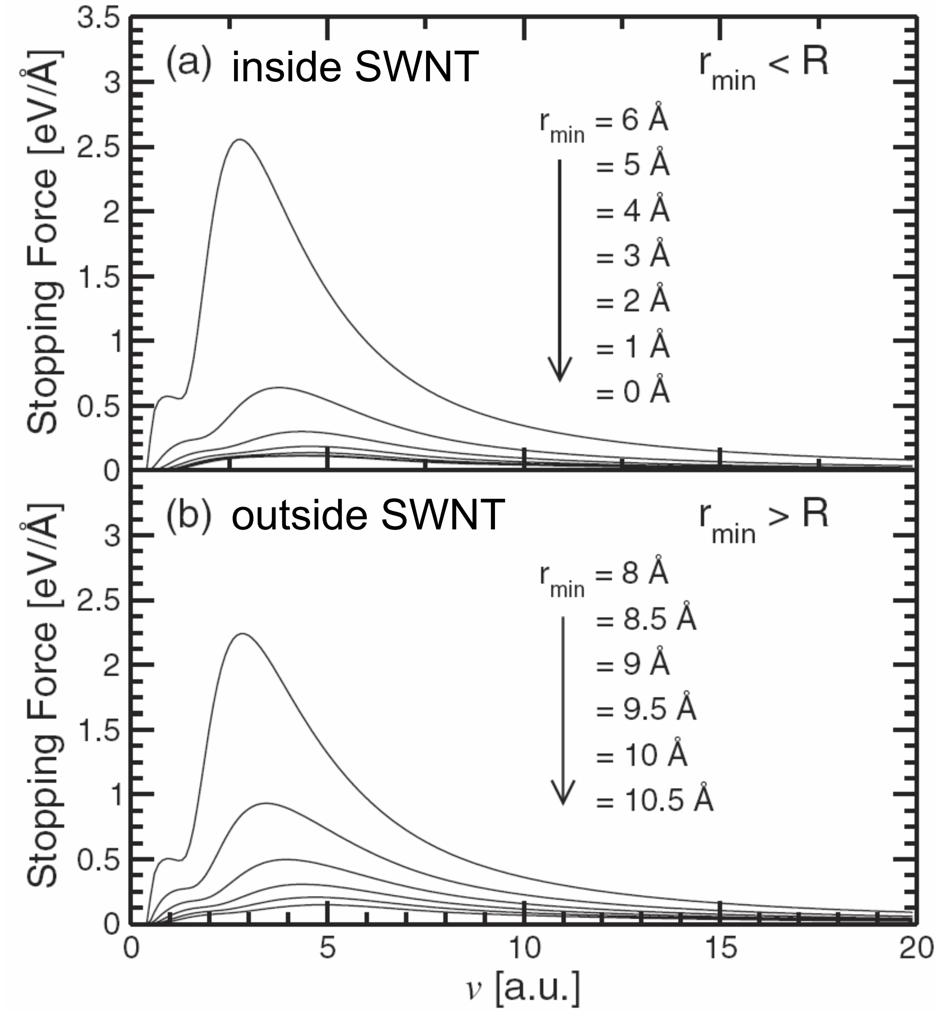

C. Kramberger, PhD thesis (2008)

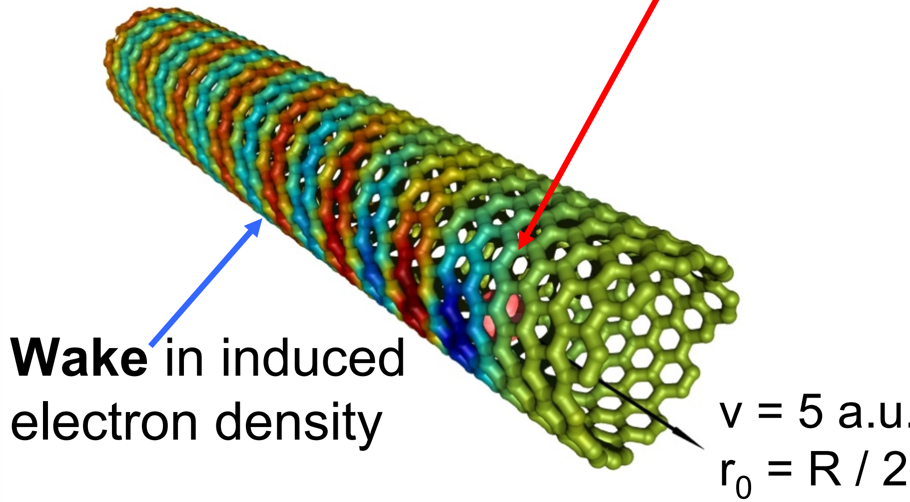


# Dynamic polarization due to **parallel** incidence of proton

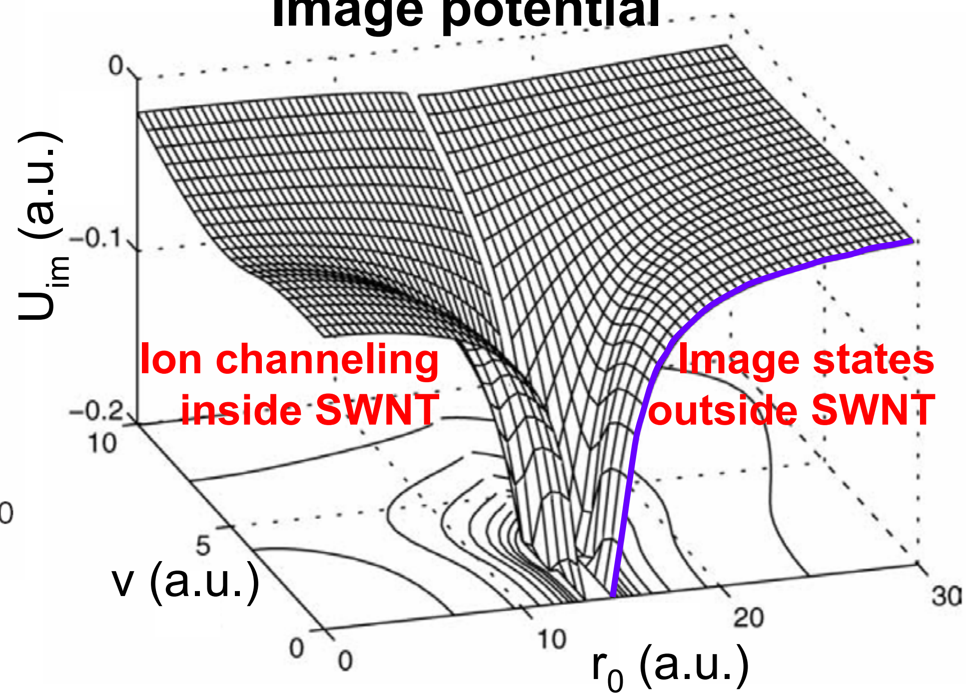
Mowbray *et al.*, *Phys. Lett.* A 320 (2004)

## Stopping power



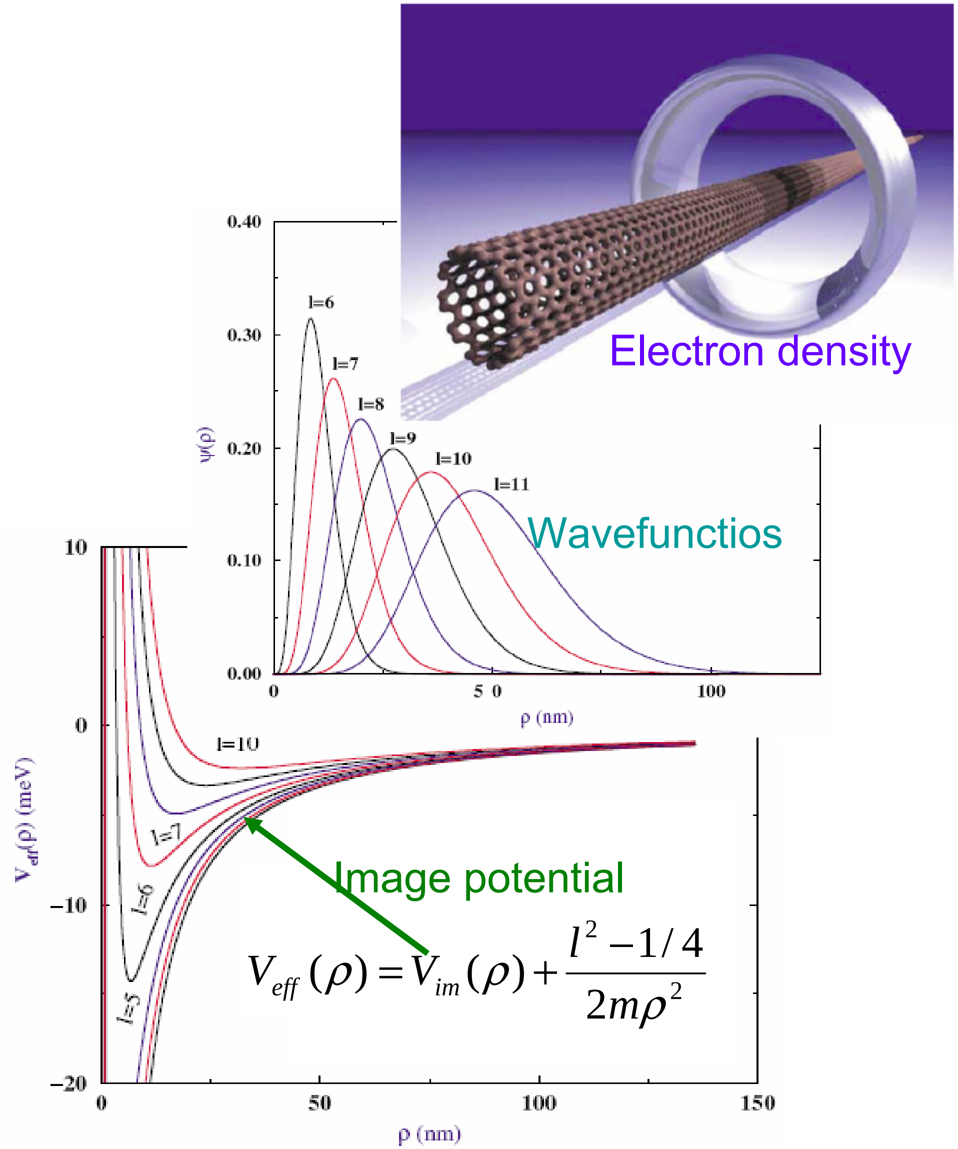

## Image potential



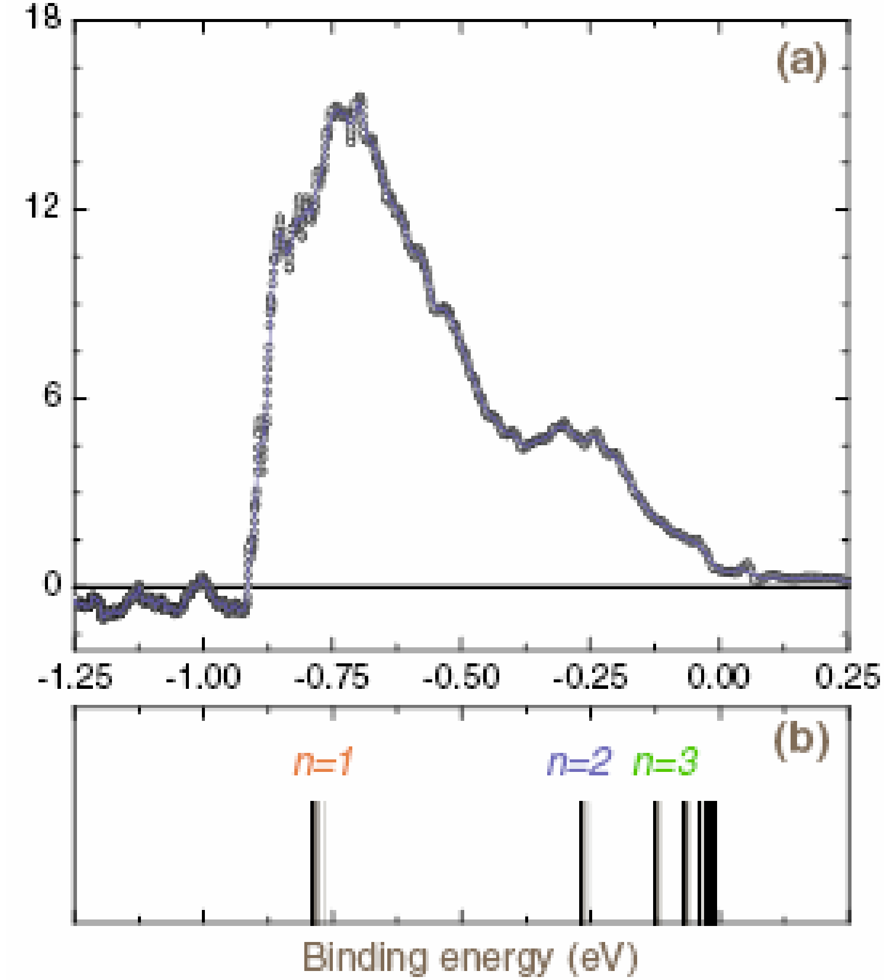
# Electron image states outside carbon nanotubes

Theoretical prediction: B.E. Granger *et al., Phys. Rev. Lett.* 89 (2002) 135506

Experimental confirmation: M. Zamkov *et al., Phys. Rev. Lett.* 93 (2004) 156803




Photoelectron signal from image state



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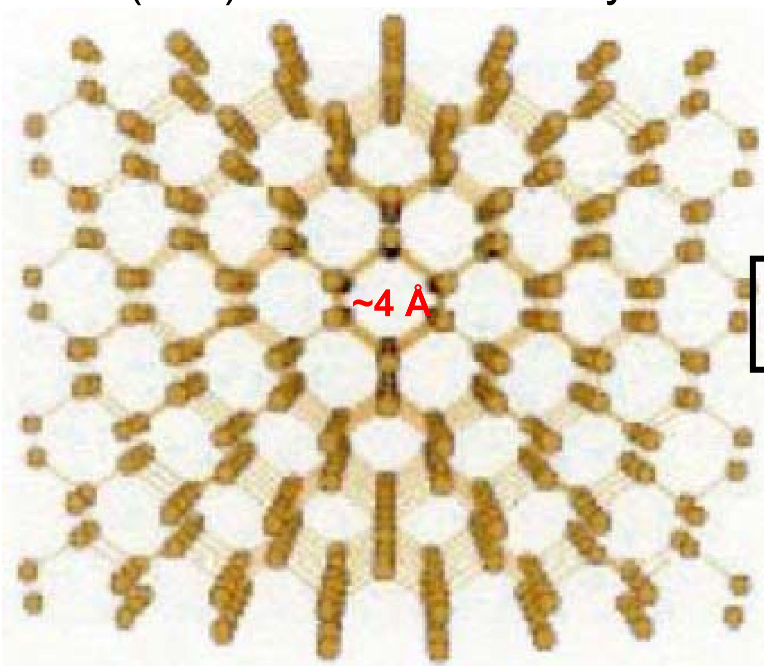
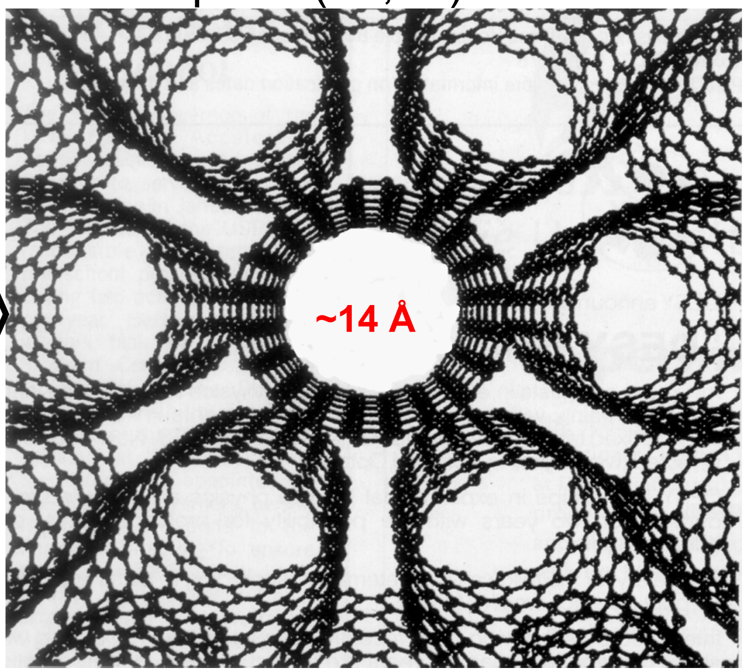
# Is **ion channeling** through carbon nanotubes feasible?

(110) channels in Si crystal

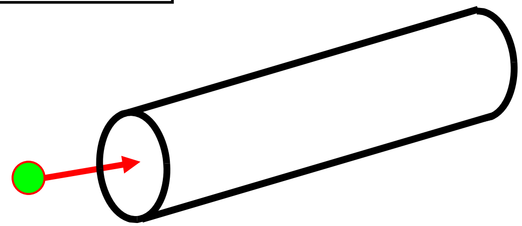



?

Rope of (10,10) SWNTs



# Ion channeling through carbon nanotubes



## Advantages over crystals

- Fewer defects
- Wider channels: weaker de-channeling
- Broader beams (using nanotube ropes)
- Wider acceptance angles (< 0.1 rad)
- Lower minimum ion energies (< 100 eV)

## Possible applications

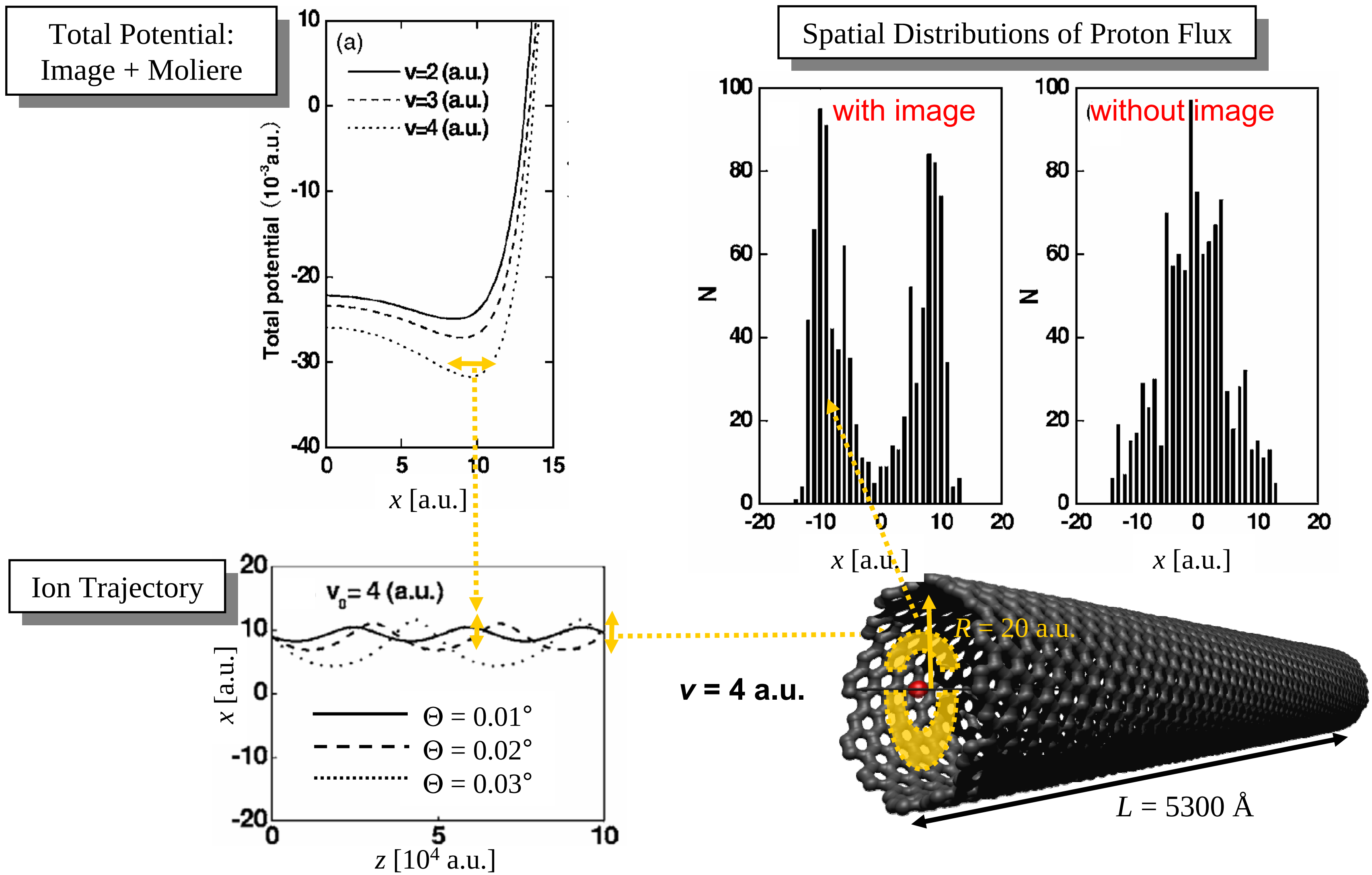
- Probing the structure of nanotubes
- Creating and transporting highly focused nano-beams
- Nano-implantation in electronics, biology & medicine
- Beam extraction, steering & collimation at accelerators

## Main problems

- Opening nanotube ends
- Amorphization of nanotube ends

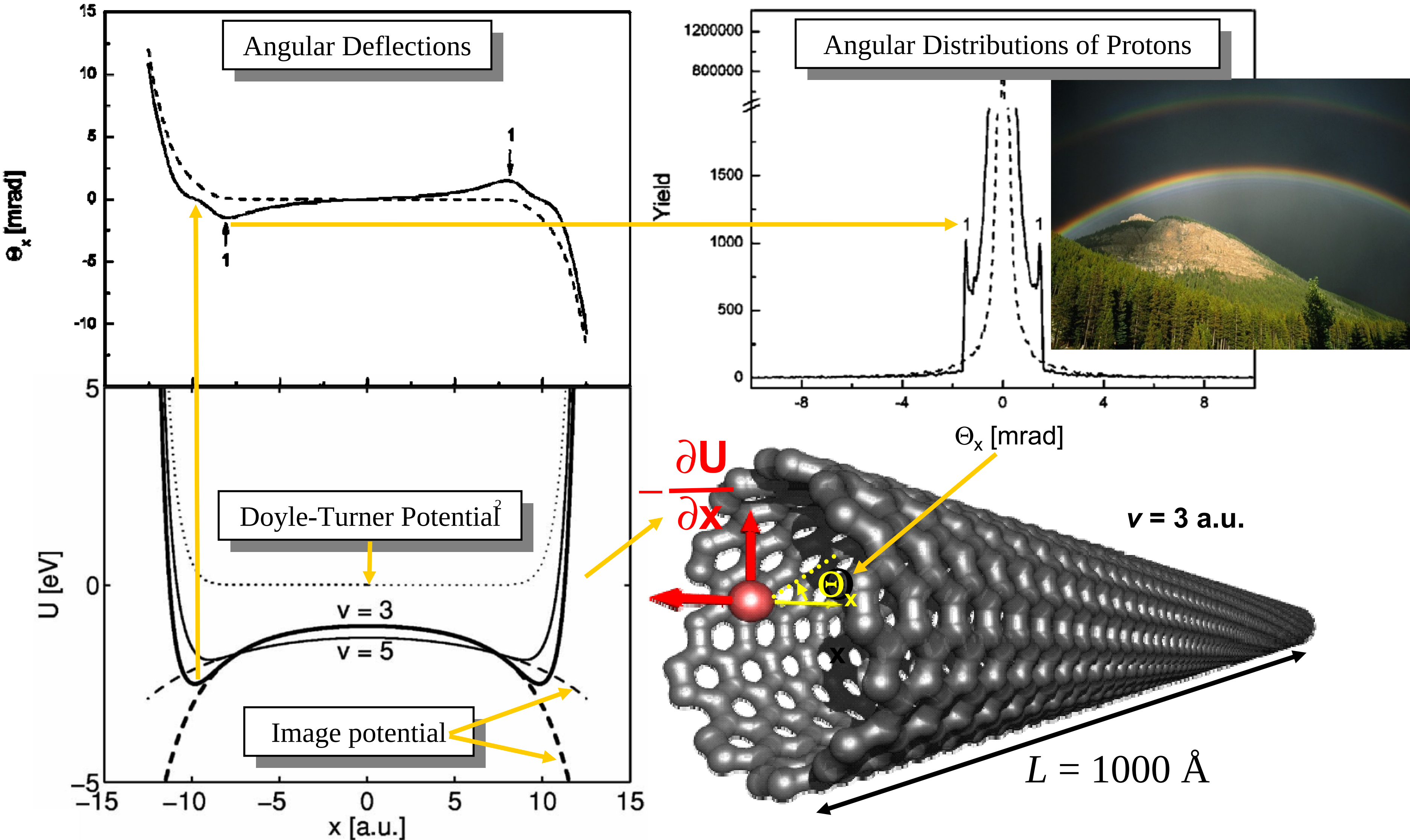
# Image-induced **hollow beam** for proton channelling inside **long** chiral SWNT

D.P. Zhou *et al.*, *Phys. Rev.* A 72 (2005) 23202



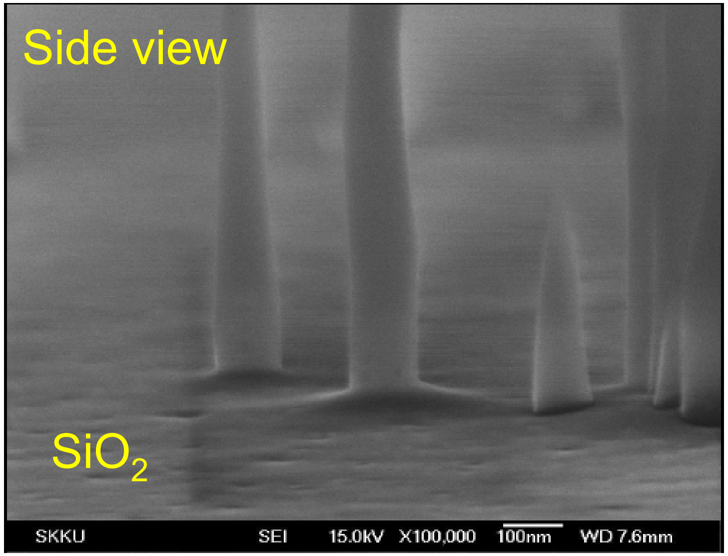
# Image-induced **rainbow effect** for proton channelling inside **short** SWNT(11,9)

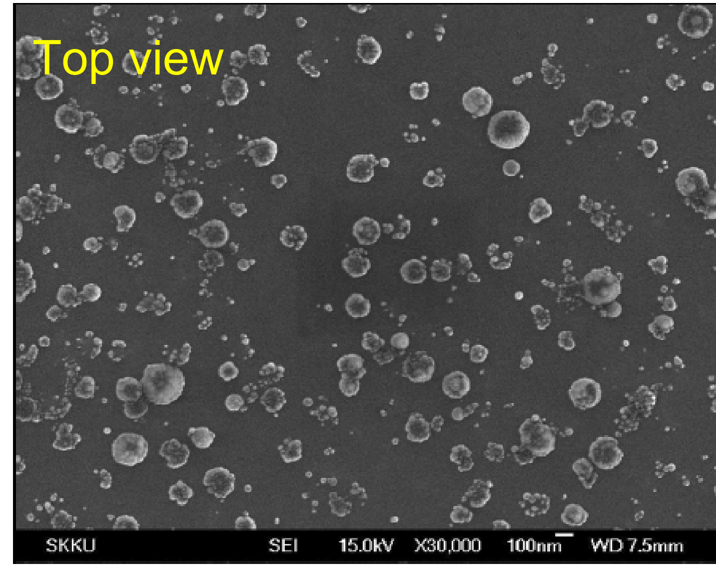
D. Borka *et al.*, *Phys. Rev.* A 73 (2006) 62902

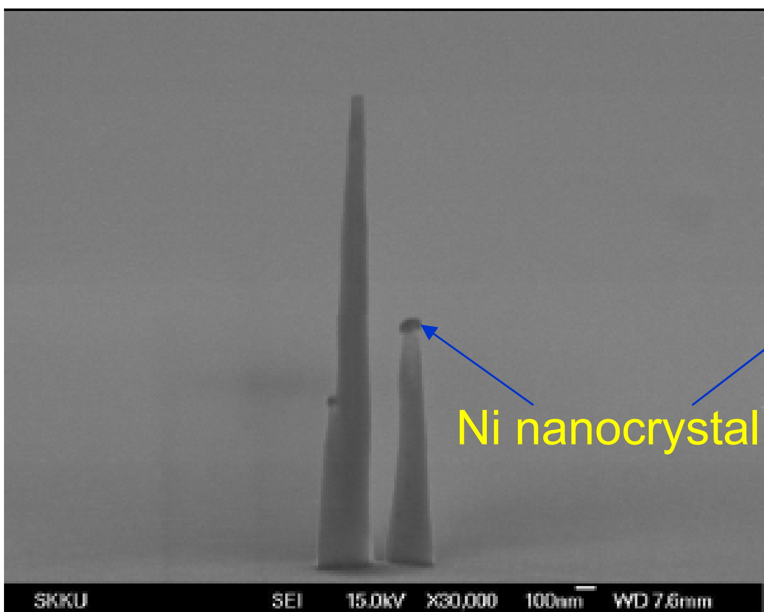


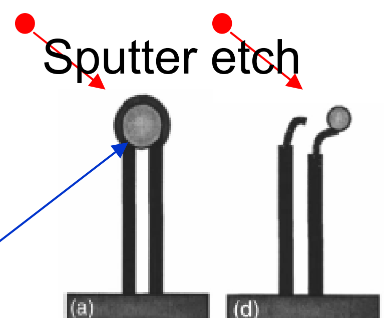
# A solution? - CNTs grown in etched ion tracks in $SiO_2$

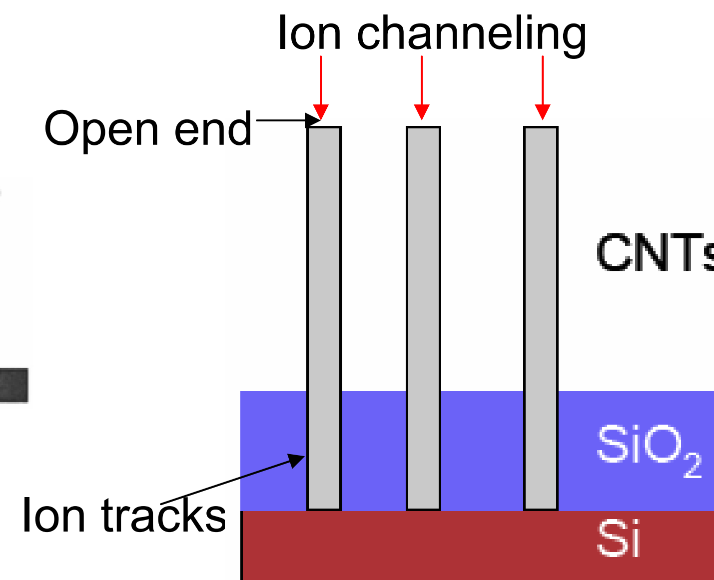
A.S. Berdinsky *et al.*, *NANO* 2 (2007) 59



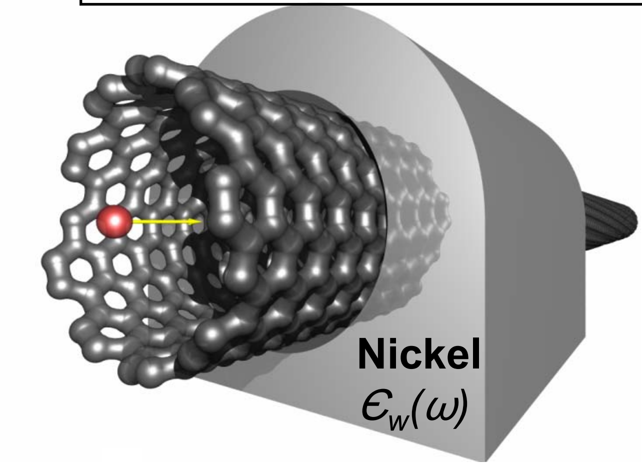



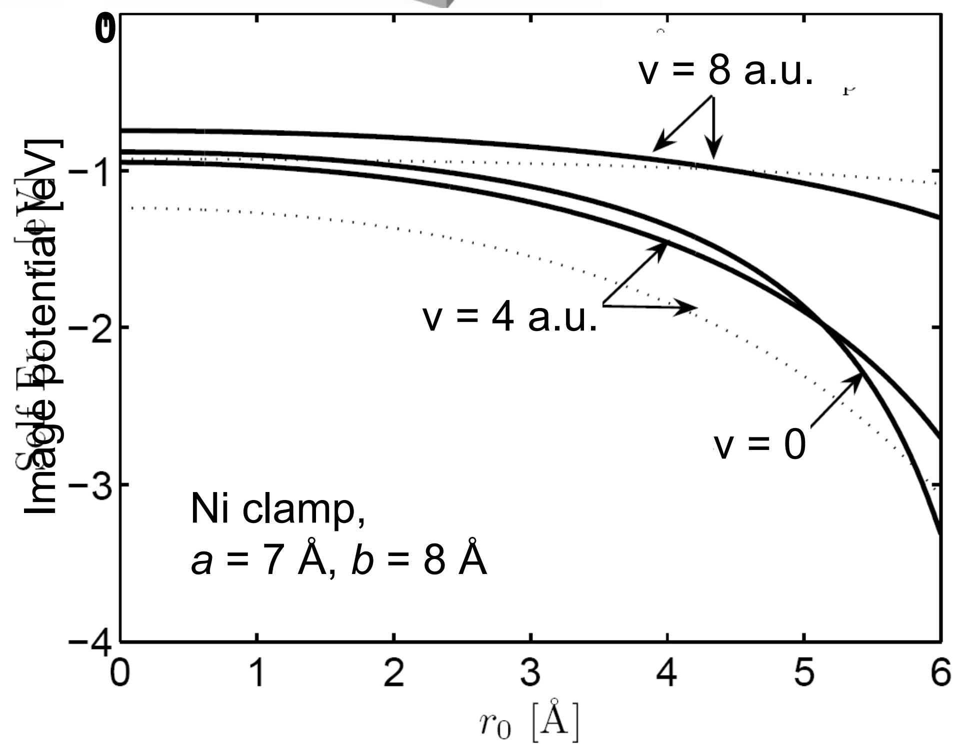
# Effect of surrounding medium on image potential

D. Mowbray *et al., Phys. Rev.* B 74 (2006) 195435




## Poisson Equation

$$\begin{aligned}\Phi(\mathbf{r},\omega) &= \Phi_{\rm ext}(\mathbf{r},\omega) + \Phi_{\rm ind}(\mathbf{r},\omega)\\ \nabla^2\Phi_{\rm ext}(\mathbf{r},\omega) &= -4\pi\rho_{\rm ext}(,\mathbf{r},\omega)\\ \nabla^2\Phi_{\rm ind}(\mathbf{r},\omega) &= 4\pi\left[n_1(\mathbf{r}_a,\omega)\delta(r-a) - \sigma_b(\mathbf{r}_b,\omega)\delta(r-b)\right]\end{aligned}$$



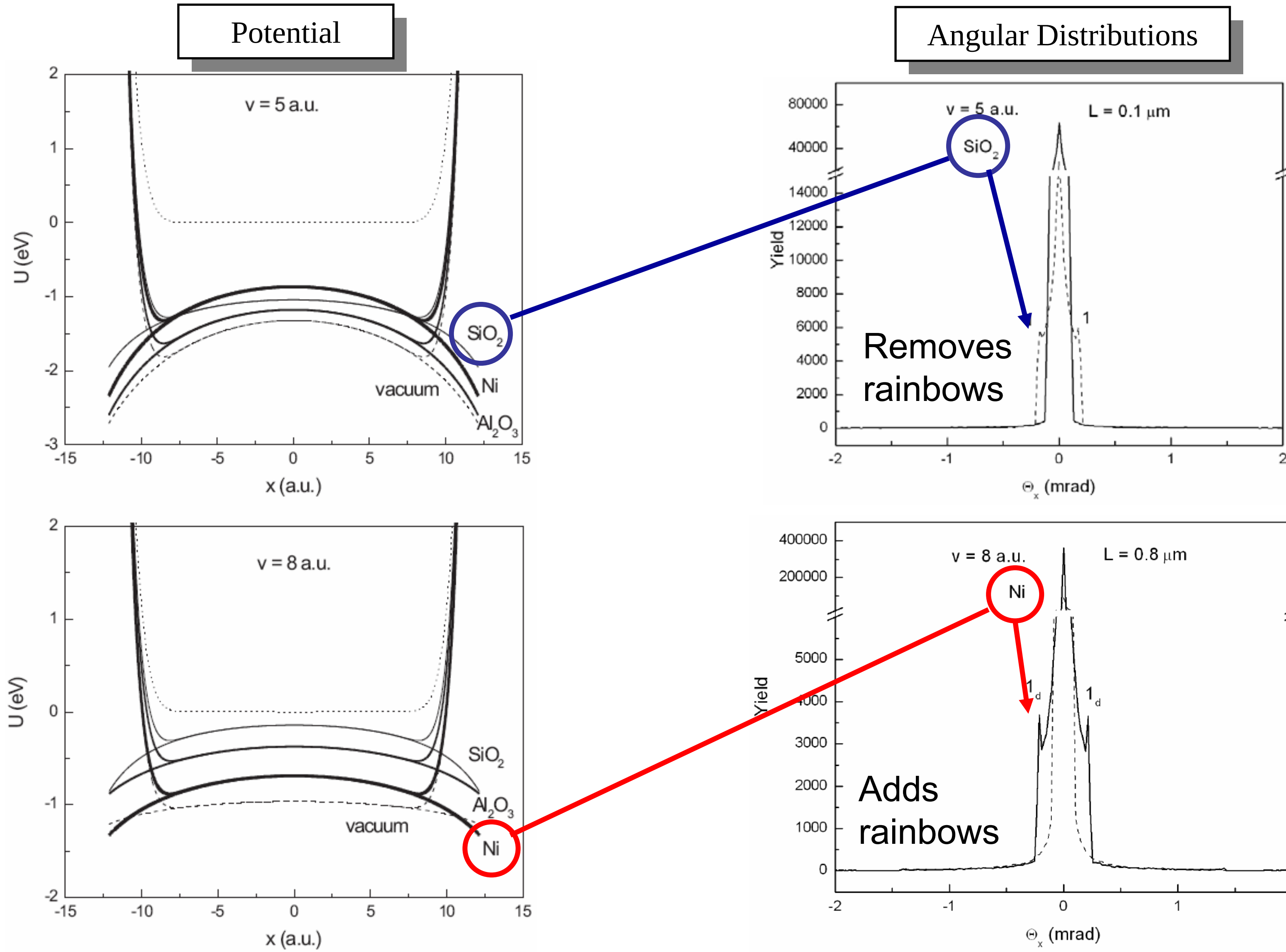

## Boundary Conditions

$$\left.\frac{\partial\Phi}{\partial r}\right|_{b+} - \left.\frac{\partial\Phi}{\partial r}\right|_{b-} = -4\pi\sigma_b(\mathbf{r}_b,\omega)$$

$$\epsilon_w(\omega)\left.\frac{\partial\Phi}{\partial r}\right|_{b+} - \left.\frac{\partial\Phi}{\partial r}\right|_{b-} = 0$$

# Effects of dielectric channel on rainbow effect for proton channelling inside **short** SWNT(11,9)

D. Borka *et al.*, *Phys. Rev.* A 77 (2008) 032903



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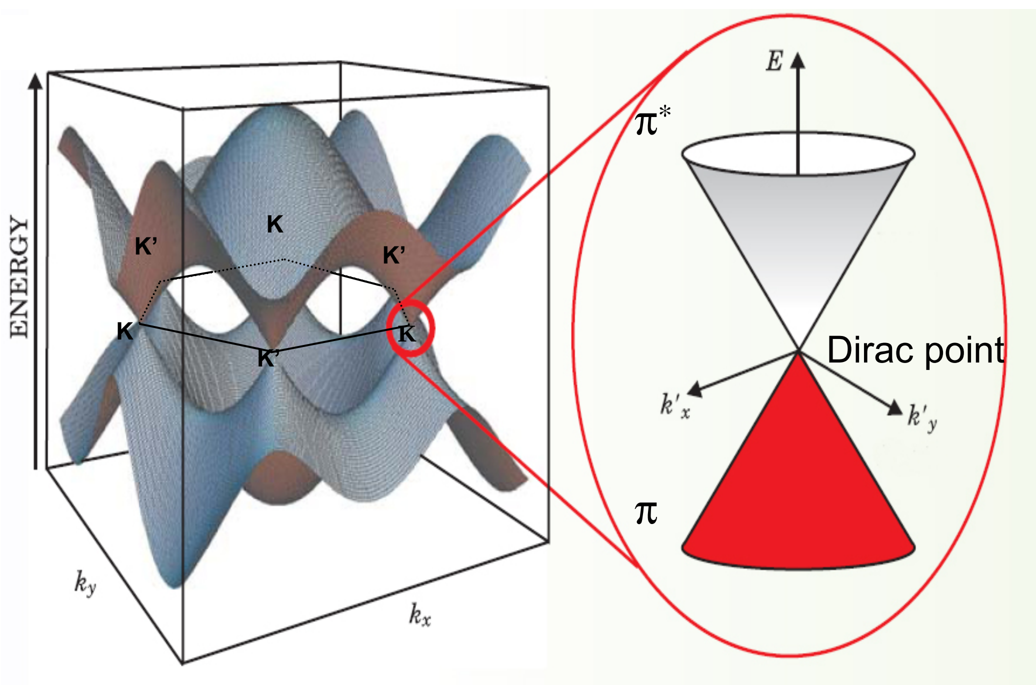
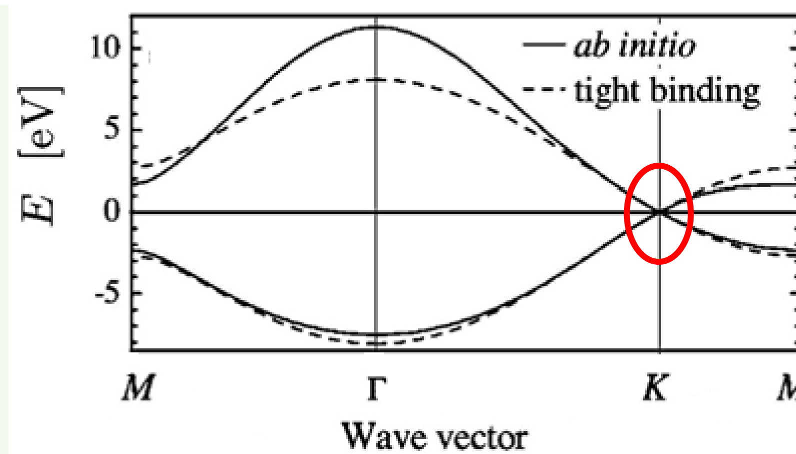
# Structure of graphene's $\pi$ - electron bands

PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

## The Band Theory of Graphite

P. R. WALLACE*
*National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario*

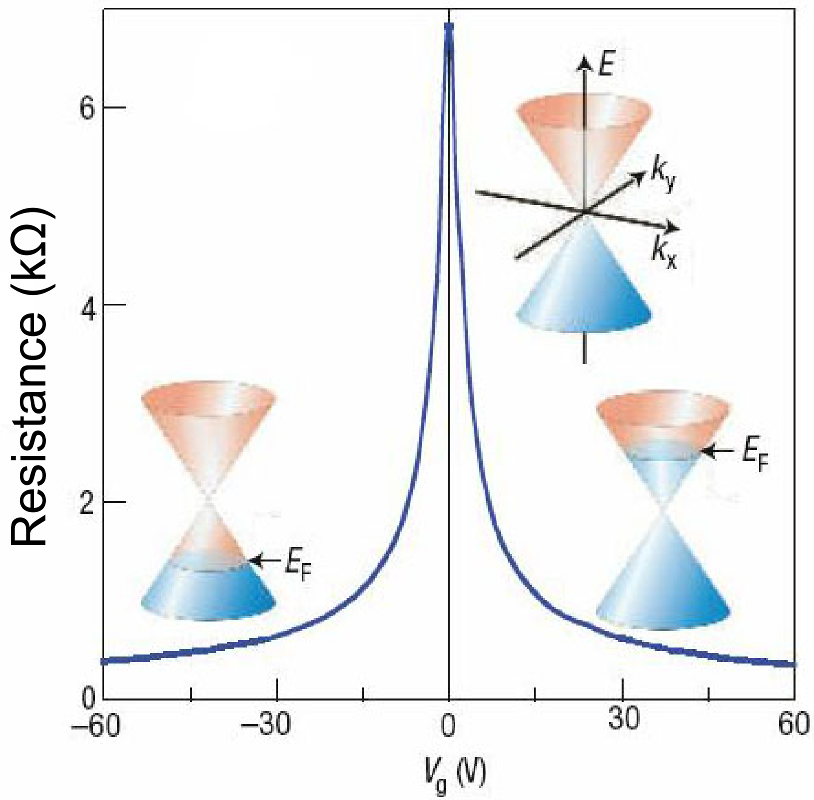


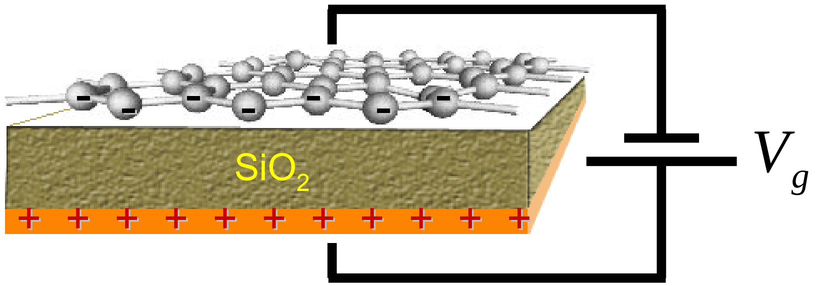

Linear DOS: $\rho(\varepsilon) \approx \dfrac{g_s g_v}{2\pi} \dfrac{|\varepsilon|}{(\hbar v_F)^2}$

Fermi speed: $v_F \approx \dfrac{c}{300}$

# Ambipolar electric field effect in single-layer graphene on top of an oxidized Si wafer

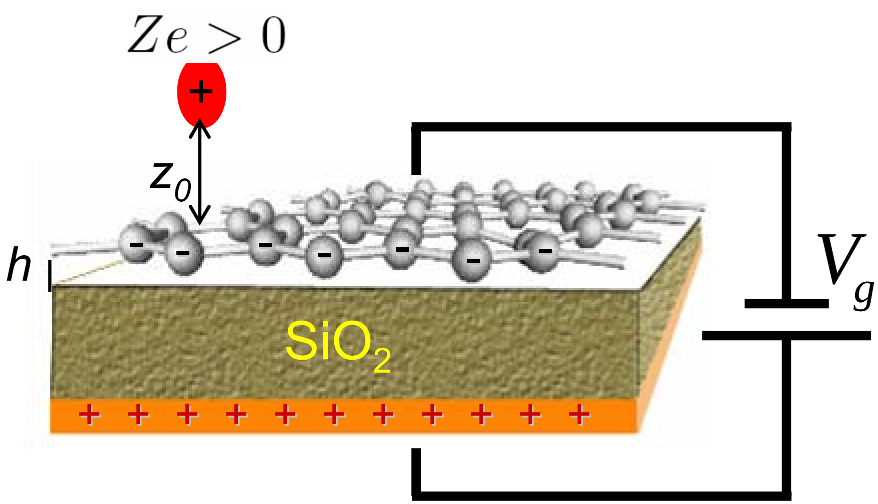



Applying **gate potential** $V_g$ shifts Fermi energy $E_F$ above or below Dirac point (electron or hole doping)

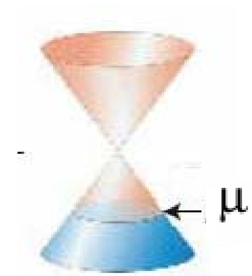


# Nonlinear screening of external charge by graphene

M. Ghaznavi *et al. Phys. Rev.* B 81 (2010) 085416




Doping gives chemical potential $\mu \gtrless 0$




Equilibrium charge carrier density $n \gtrless 0$

$$n(\mu) = \int_0^\infty d\varepsilon\, \rho(\varepsilon) \left[ \frac{1}{1 + \mathrm{e}^{\beta(\varepsilon - \mu)}} - \frac{1}{1 + \mathrm{e}^{\beta(\varepsilon + \mu)}} \right]$$

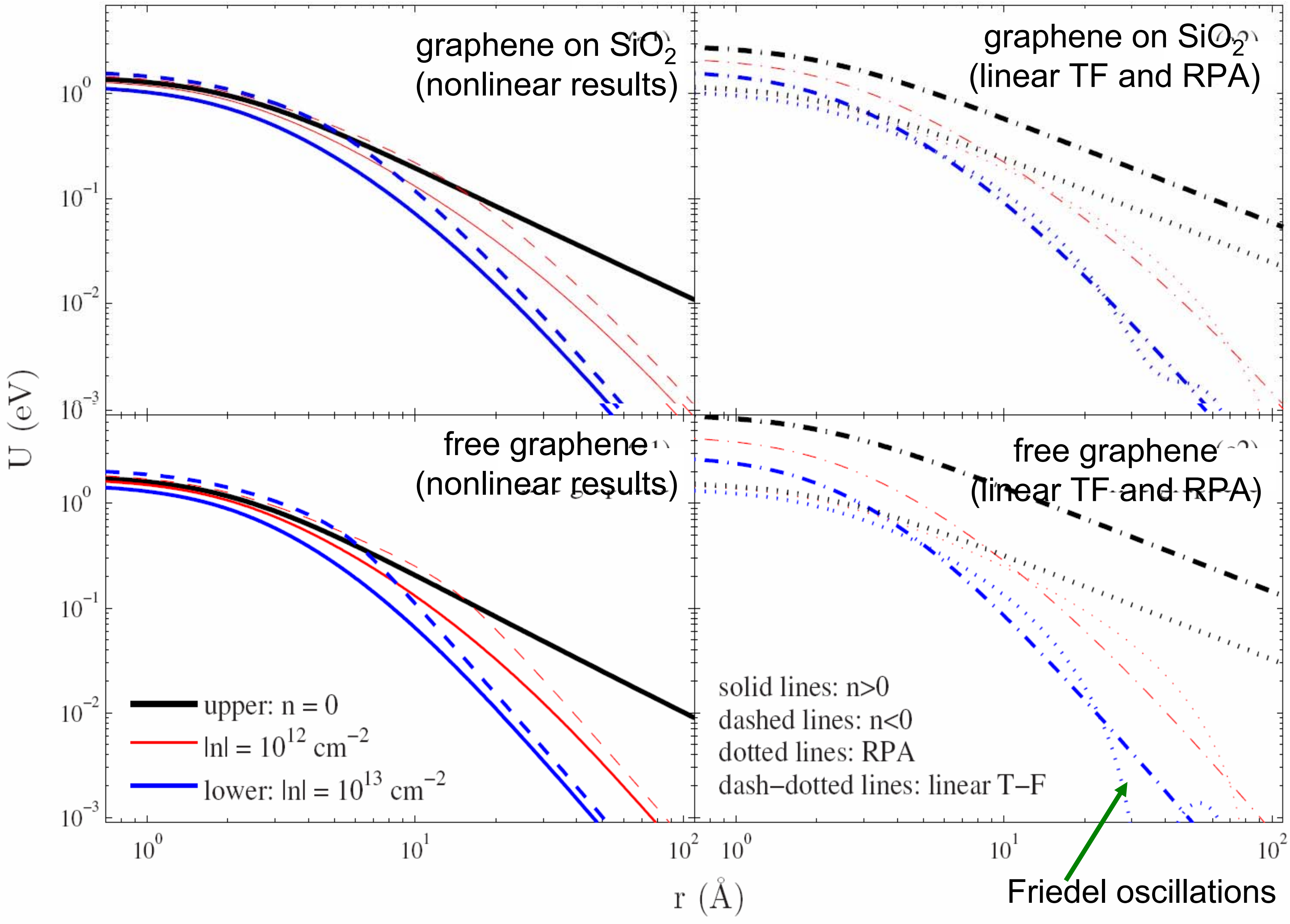
Thomas-Fermi model at finite $T$

$$U(\mathbf{r}) = U_{\mathrm{ext}}(\mathbf{r}) - e^2 \int d^2\mathbf{r}' \left[ n\left(\mu + U(\mathbf{r}')\right) - n\left(\mu\right) \right] \left[ \frac{1}{\|\mathbf{r} - \mathbf{r}'\|} - \frac{\epsilon_{\mathrm{s}} - 1}{\epsilon_{\mathrm{s}} + 1} \frac{1}{\sqrt{(\mathbf{r} - \mathbf{r}')^2 + 4h^2}} \right]$$

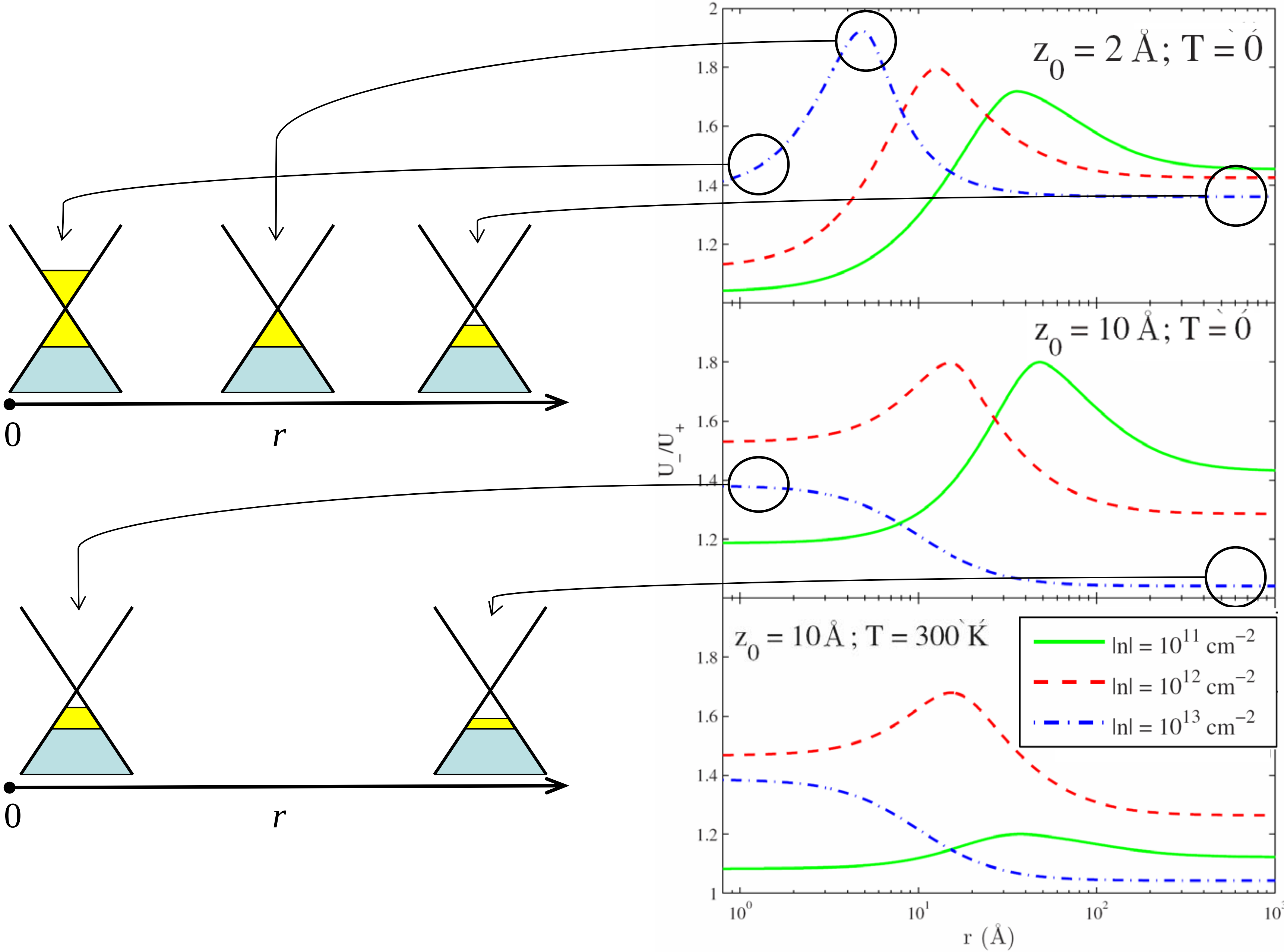
Self-consistent solution for screened potential $U_{\pm}(r)$ in graphene when $\mu \gtrless 0$

# Screened potential in graphene due to external charge

M. Ghaznavi *et al. Phys. Rev.* B 81 (2010) 085416



# Ratio $U_-(r)/U_+(r)$ of screened potentials for $n \lessgtr 0$



# Nonlinear image interaction for external charge

M. Ghaznavi *et al. Phys. Rev.* B 81 (2010) 085416

Image force in terms of effective dielectric constant

$$F_{im} = \frac{(Ze)^2}{4z_0^2}\left[\frac{1}{\varepsilon_*(z_0)} - 1\right]$$

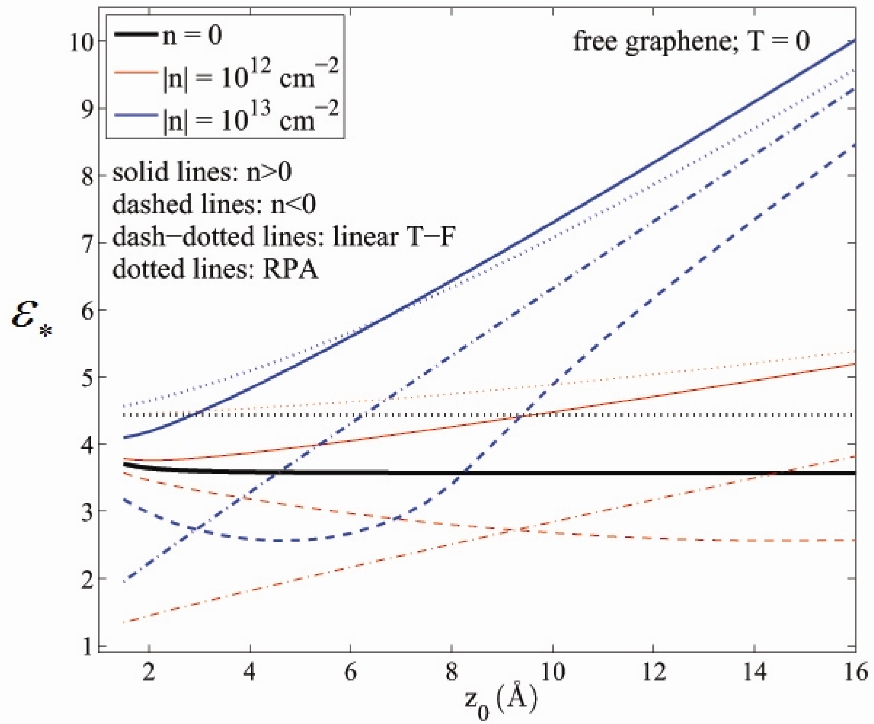
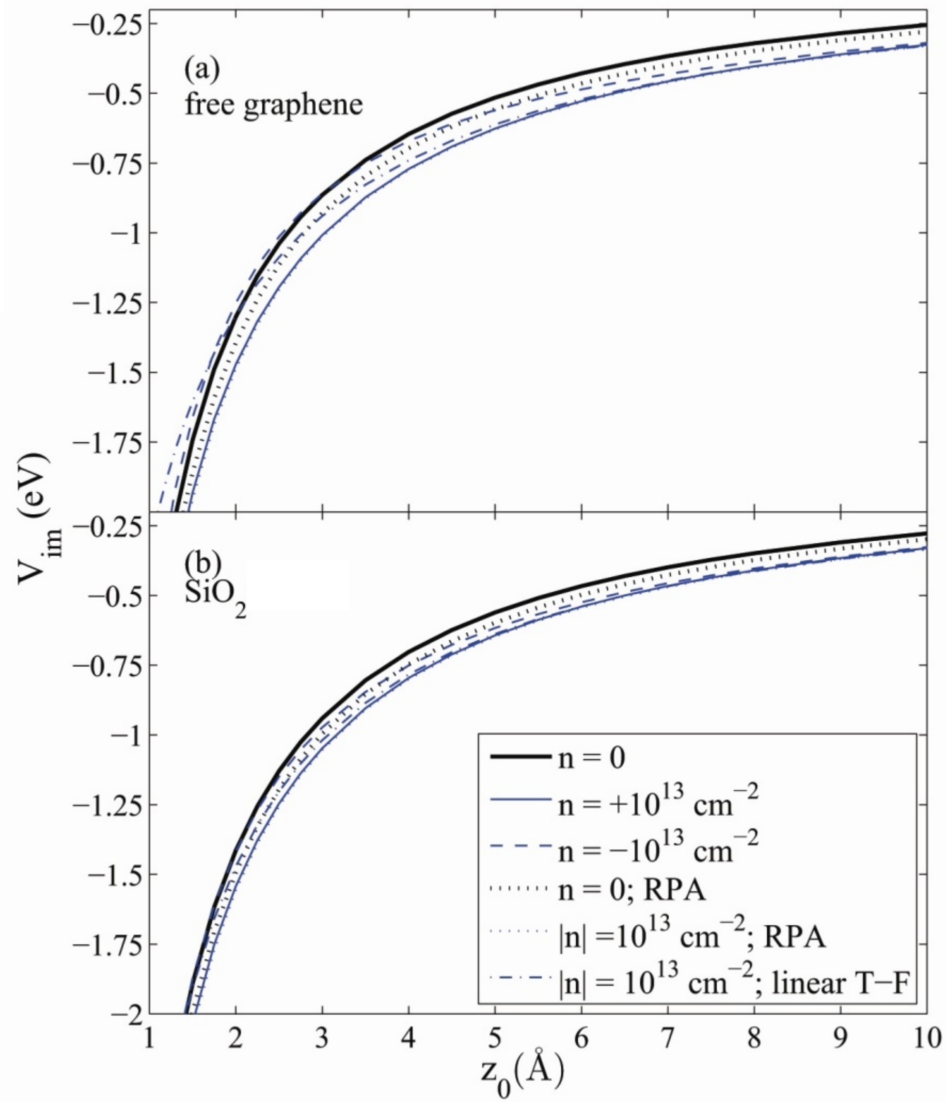



Image potential



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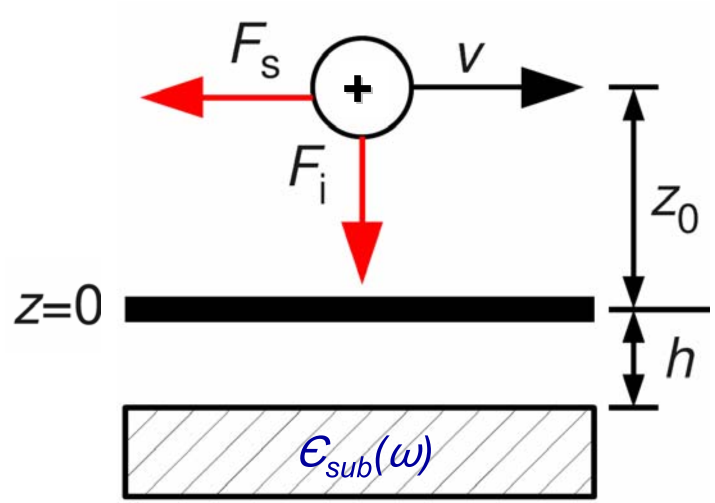
# Interaction of moving external charge with graphene

K.F. Allison *et al.*,*Phys. Rev.* 80 (2009), *Nanotechnology* 21 (2010) 134017




## Study several effects:

- doping via gate potential
- damping via Mermin approach
- local field effects
- phonons in polar substrate
- size of gap to the substrate

Dielectric function of graphene + substrate: Random Phase Approximation

$$\epsilon(q,\omega) = \left[1 - \frac{\epsilon_{\text{sub}}(\omega) - 1}{\epsilon_{\text{sub}}(\omega) + 1}\,\mathrm{e}^{-2qh}\right]^{-1} + \frac{2\pi e^2}{q}\Pi_{\text{gra}}(q,\omega;\gamma)$$

Stopping force

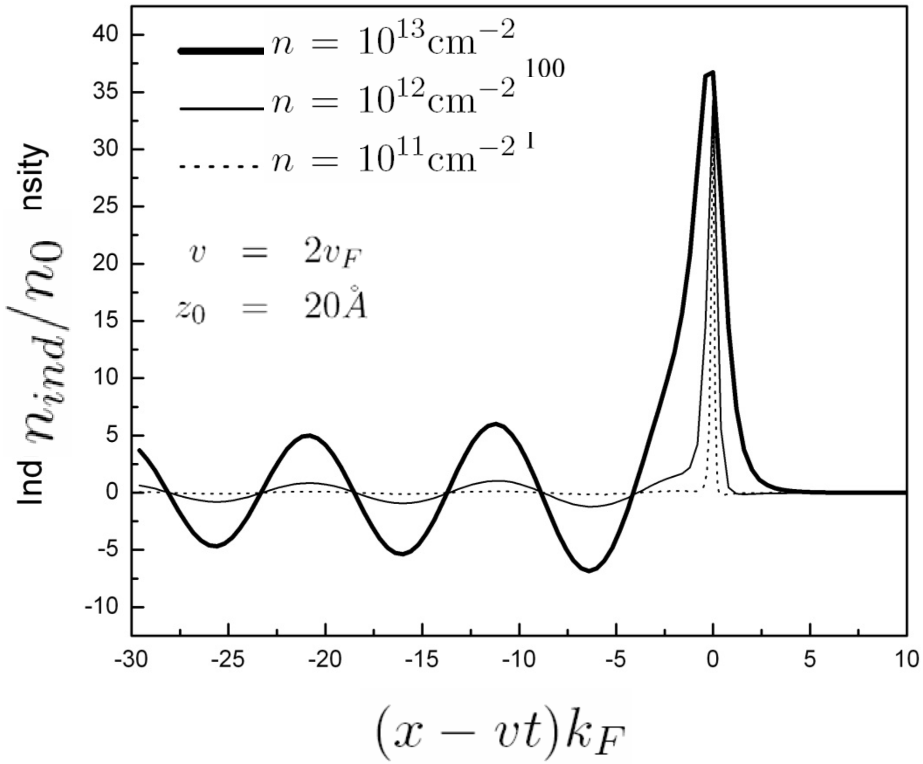
$$F_s = \frac{2}{\pi}\frac{Z^2e^2}{v}\int_0^\infty dq e^{-2qz_0}\int_0^{qv} d\omega \frac{\omega}{\sqrt{q^2v^2 - \omega^2}}\Im\left[\frac{1}{\epsilon(q,\omega)}\right]$$

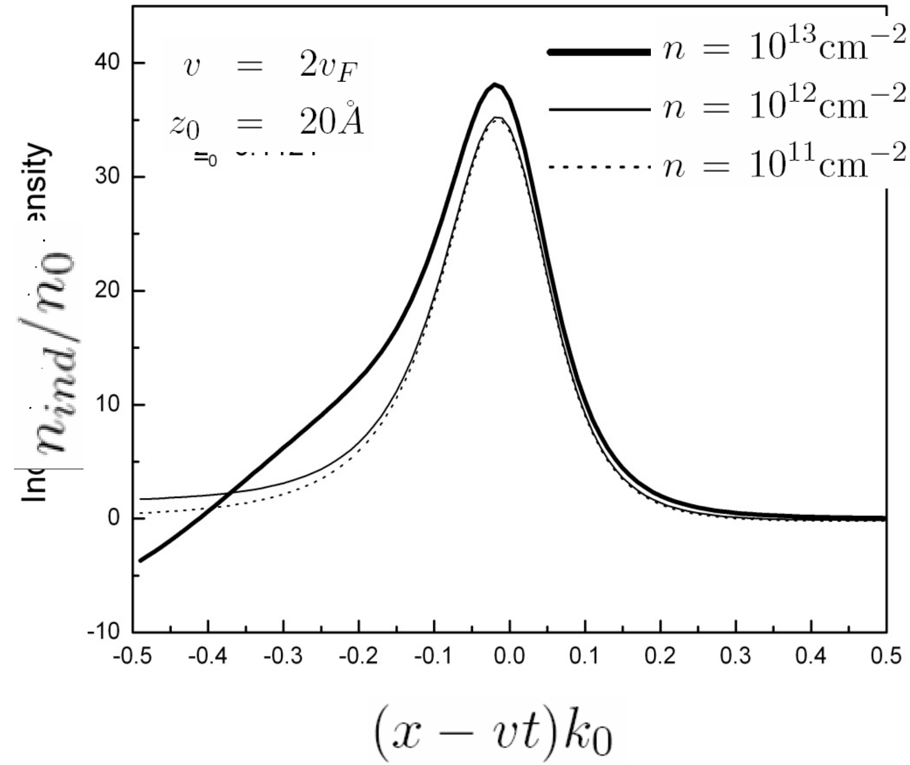
Image force

$$F_i = \frac{2}{\pi}Z^2e^2\int_0^\infty dq q e^{-2qz_0}\int_0^{qv} \frac{d\omega}{\sqrt{q^2v^2 - \omega^2}}\Re\left[\frac{1}{\epsilon(q,\omega)} - 1\right]$$

# Wake effect due to charge moving over free graphene

$$n_0 = 10^{11}\ \mathrm{cm}^{-2}$$




$$k_F = \sqrt{\pi n}$$

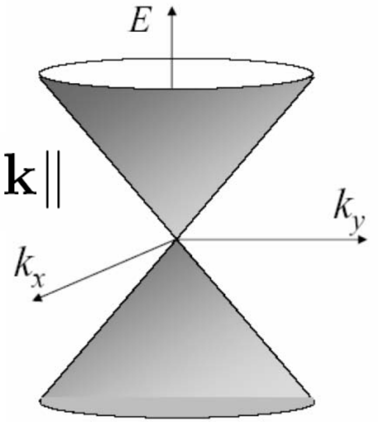
$$k_0 = \sqrt{\pi n_0}$$

# Loss Function $-\Im\{1/\epsilon(q,\omega)\}$ for graphene and 2DEG

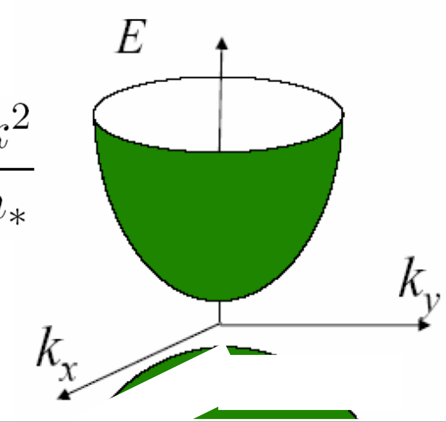
$$\varepsilon_{\mathbf{k}} = \hbar v_F \|\mathbf{k}\|$$

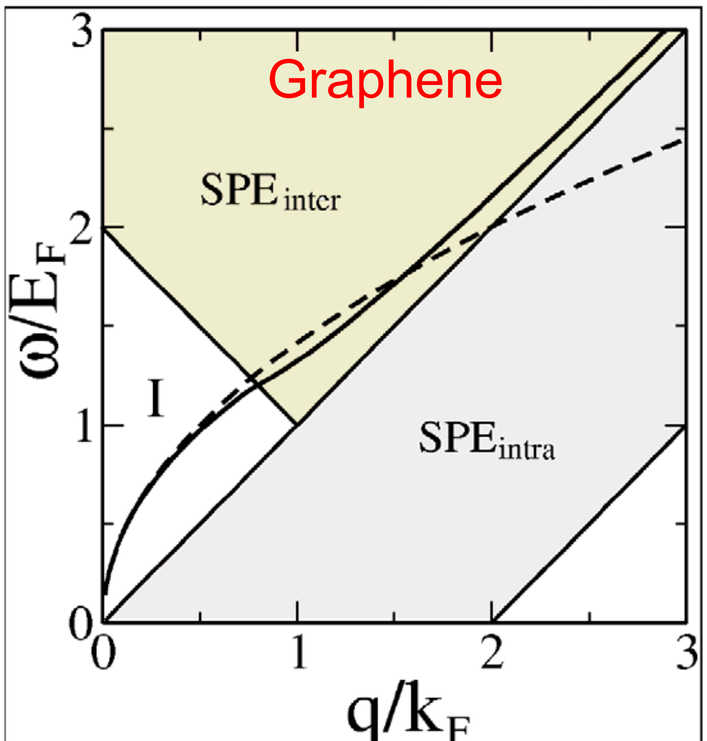
$$E_F = \hbar v_F k_F$$

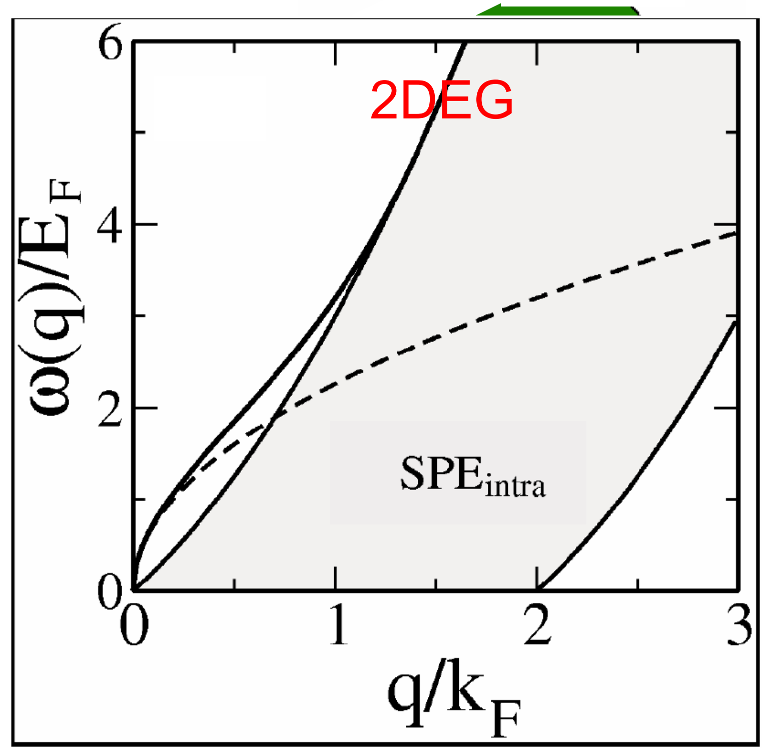
$$k_F = \sqrt{\pi n}$$

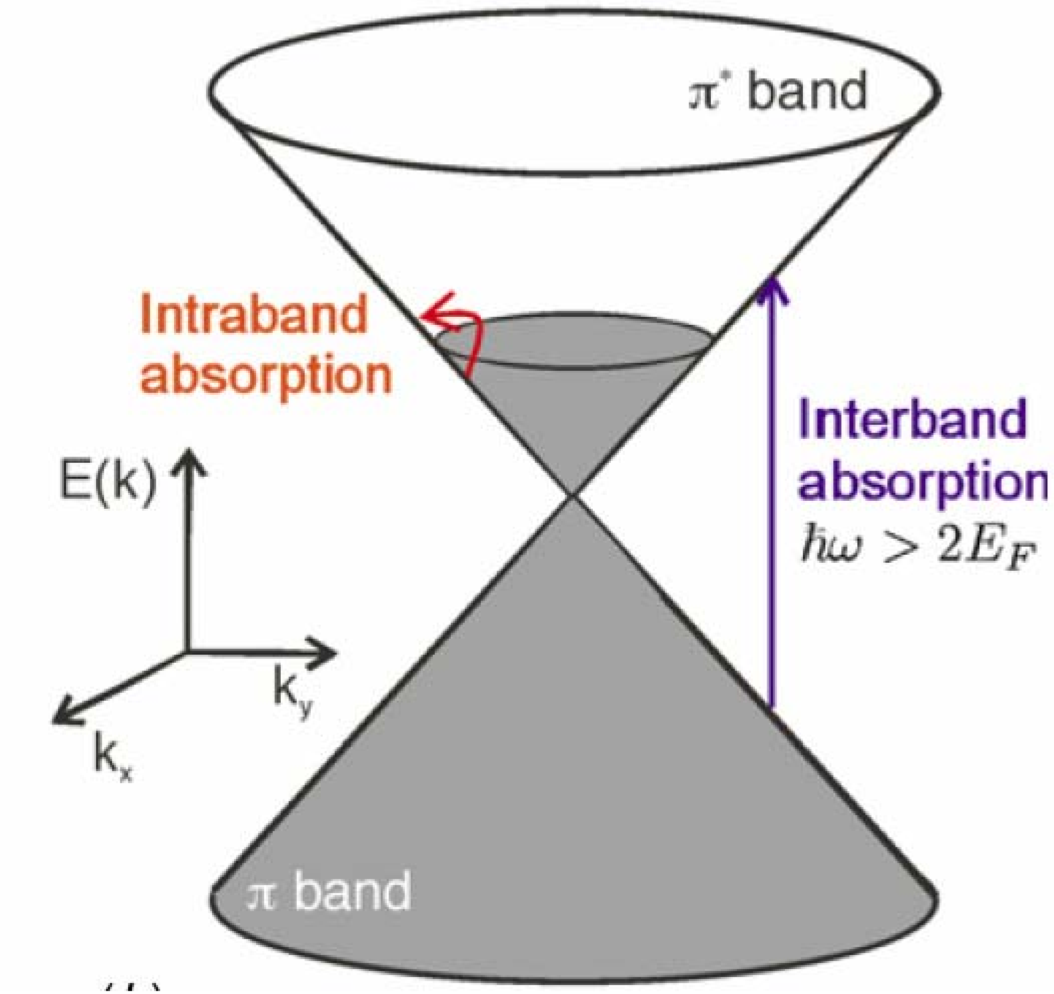



$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m_*}$$



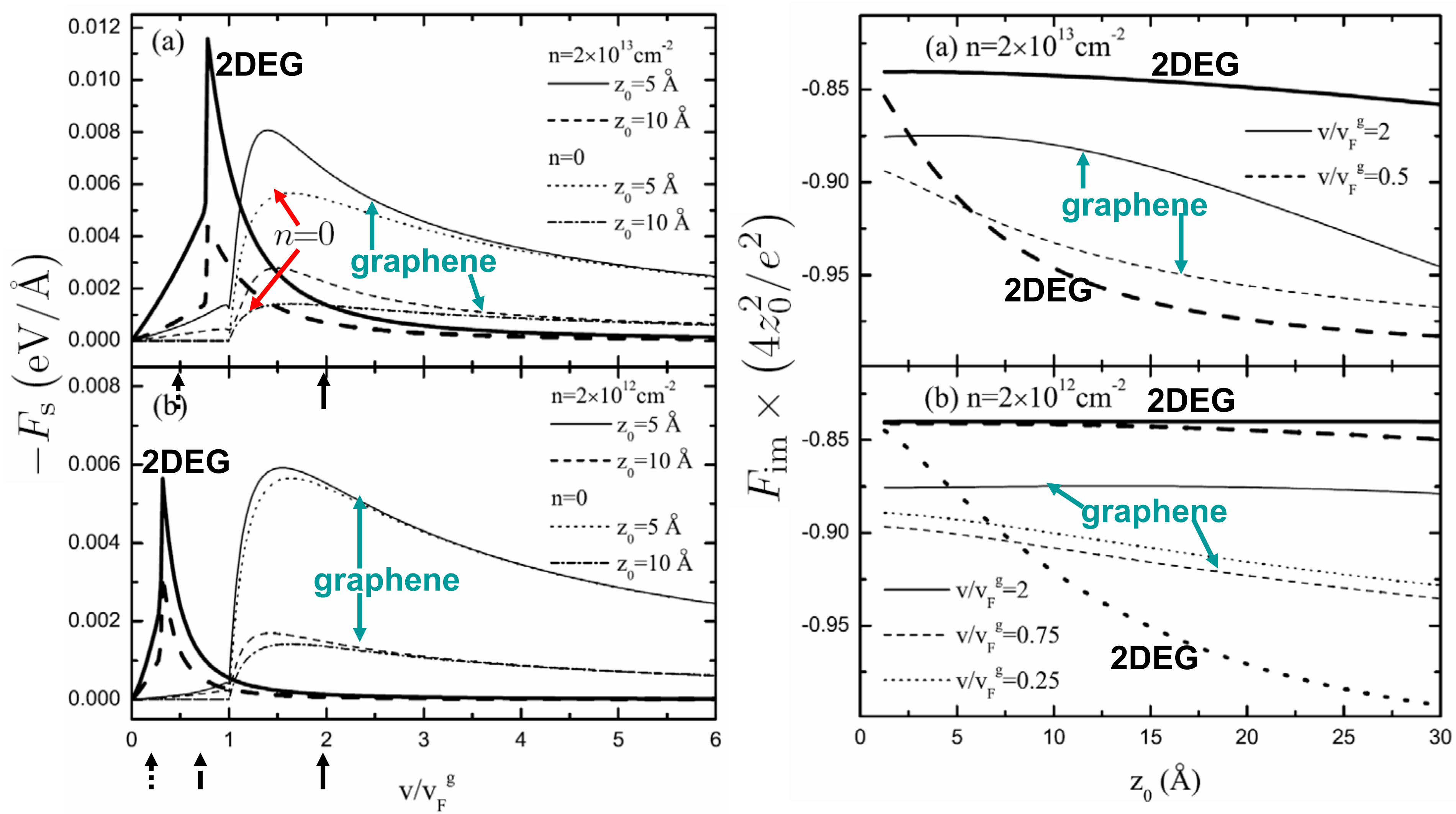


$\pi^*$ band
Intraband absorption
Interband absorption
$\hbar\omega > 2E_F$
E(k)
$k_y$
$k_x$
$\pi$ band

# Stopping and image forces on a point charge moving over epitaxial graphene on SiC and 2DEG (Ag on Si)

Stopping force vs. speed

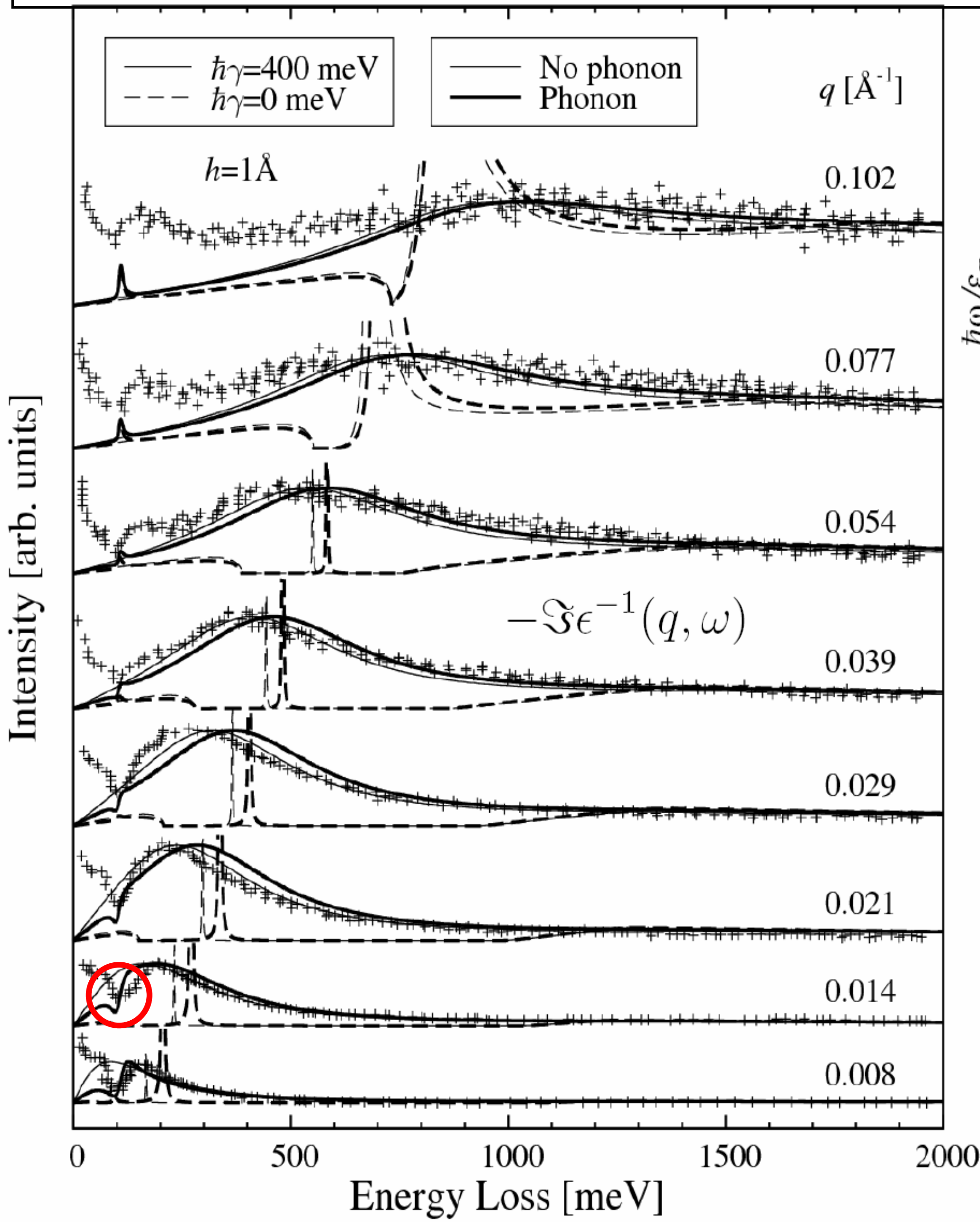
Image force (normalized) vs. distance

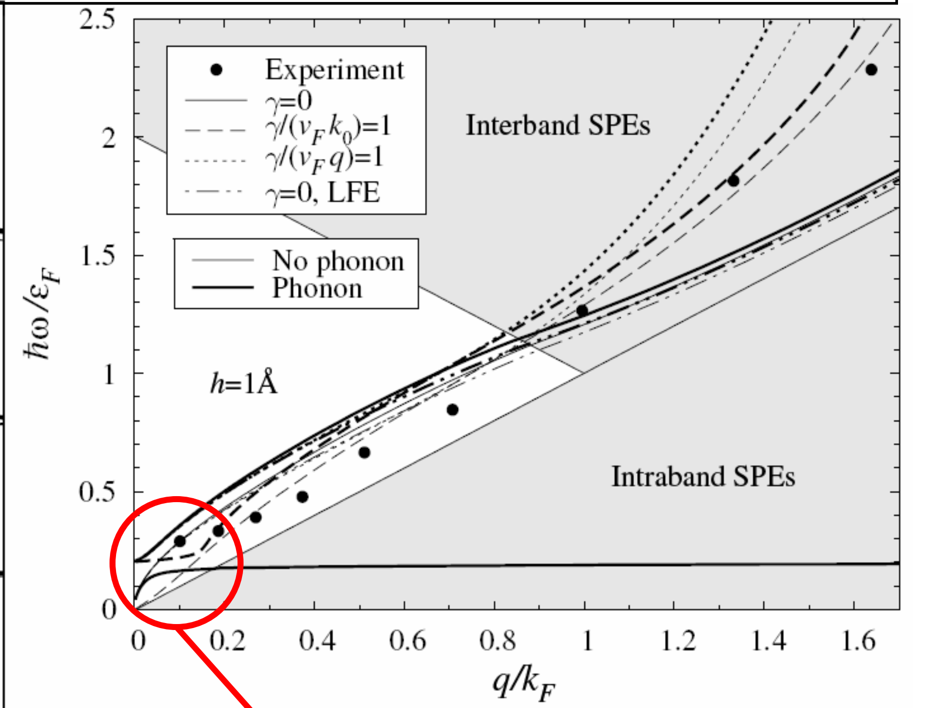


# Outline

- ❑ Introduction
- ❑ Interactions of fast ions with CNTs
  - Plasmon excitations: oblique incidence
  - Ion channeling: rainbow effect
- ❑ Interactions of slow ions with graphene
  - Nonlinear static screening
  - Dynamic screening: wake, stopping, image
  - Plasmon hybridization with substrate phonons
- ❑ Outlook

# **HREELS spectra for graphene on SiC,** exper. by Liu *et al.* PRB 78 (2008) 201403



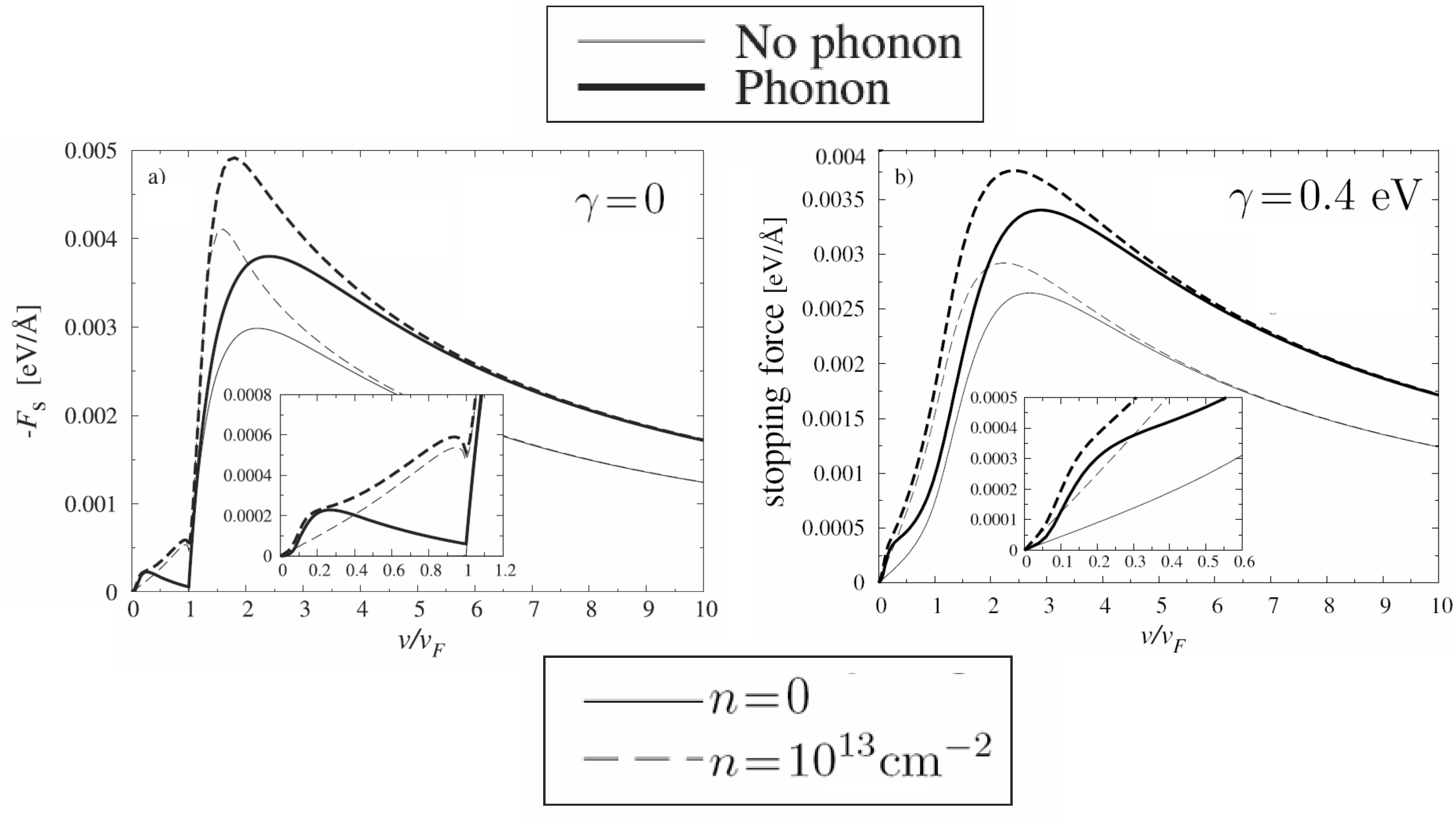

Plasmon coupling with substrate phonon

$$\epsilon(q,\omega) \approx 1 + \epsilon_{\mathrm{sub}}(\omega) - 4\frac{e^2}{\hbar}\frac{v_F q}{\omega^2}\sqrt{\pi n} = 0$$

$$\epsilon_{\mathrm{sub}}(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\frac{\omega_{\mathrm{TO}}^2}{\omega_{\mathrm{TO}}^2 - \omega^2}$$

# Effects of substrate phonons and plasmon damping on stopping force for protons above graphene on SiC

K.F. Allison *et al.*, *Nanotechnology* 21 (2010) 134017



# Outlook

- Electronic energy loss important part of charged particle interactions with carbon nanostructures: energy deposition & transport through target
- Plasmon excitations at aloof trajectories: full theory needed for dielectric response of both $\sigma$ and $\pi$ electrons
- Image interaction and electronic energy loss for: ion channeling in CNTs and grazing scattering on graphene
- Effects of dielectric environment
- Concept of friction
- Ion charge states

Thank you for your attention

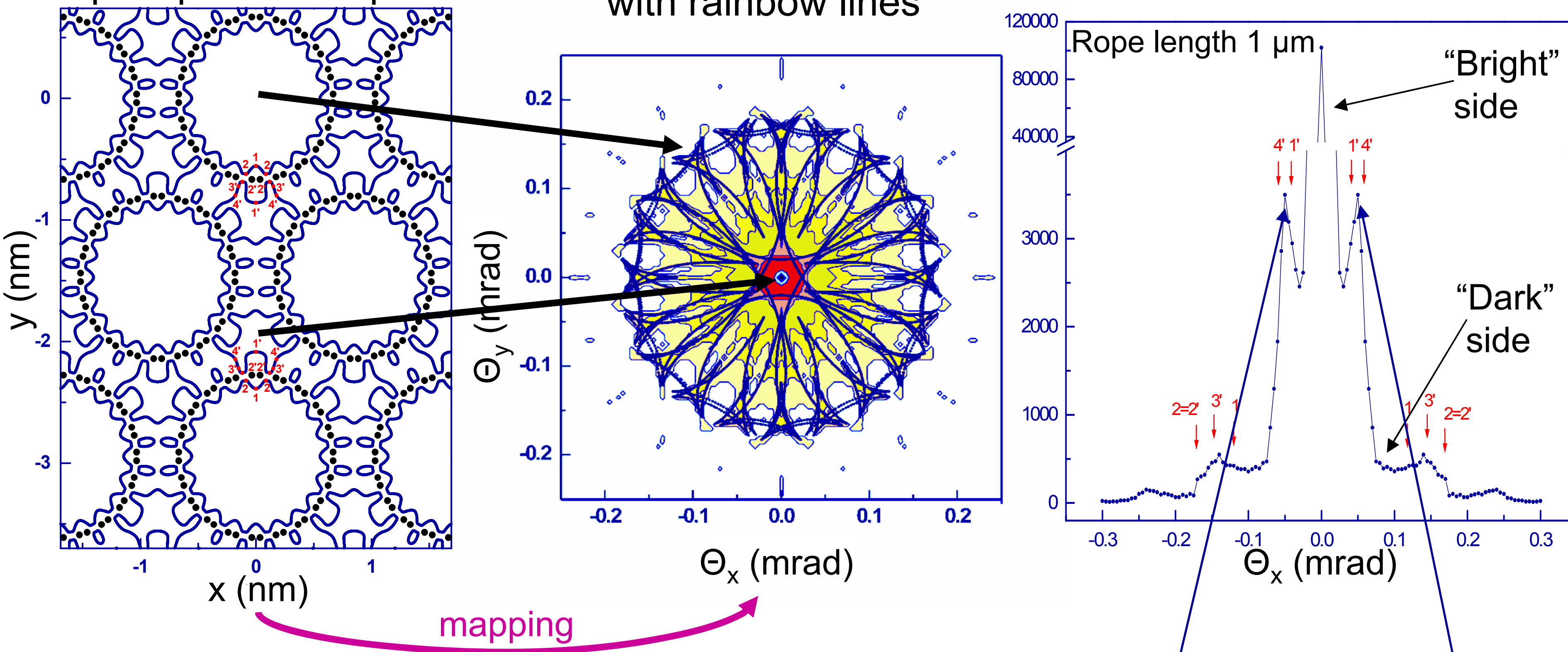
# **Rainbow effect** after 1GeV proton channelling through a **short** rope of SWNTs(10,10)

S. Petrovic *et al.*, *Eur. Phys. J.* B 44 (2005) 41

Rainbow lines in the impact parameter plane

Angular distribution with rainbow lines

Yield of protons along $\Theta_x$ line

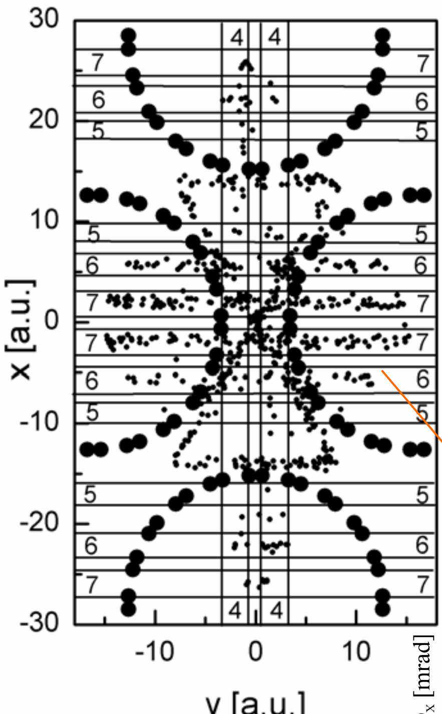



Jacobian: $J \equiv \partial_x \Theta_x \partial_y \Theta_y - \partial_x \Theta_y \partial_y \Theta_x$ , cross-section: $\sigma = 1/|J|$ , Rainbow peaks from $J = 0$

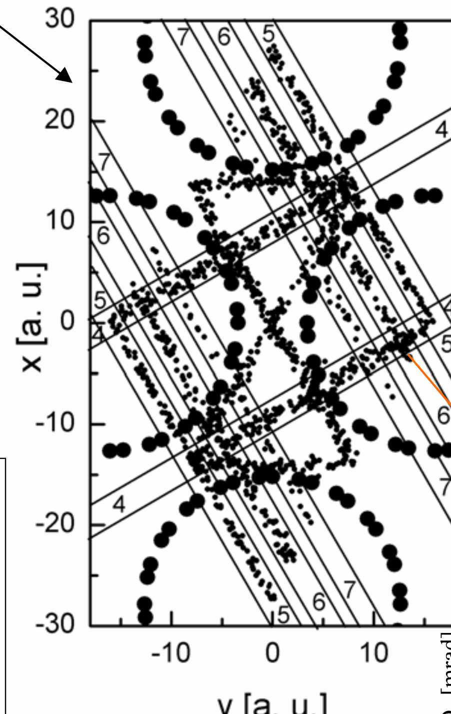
# **Star effect** in channeling of divergent 1GeV proton beam through **long** ropes of SWNTs(10,10)

D. Borka *et al., Nucl. Instr. Meth* A 354 (2006) 457

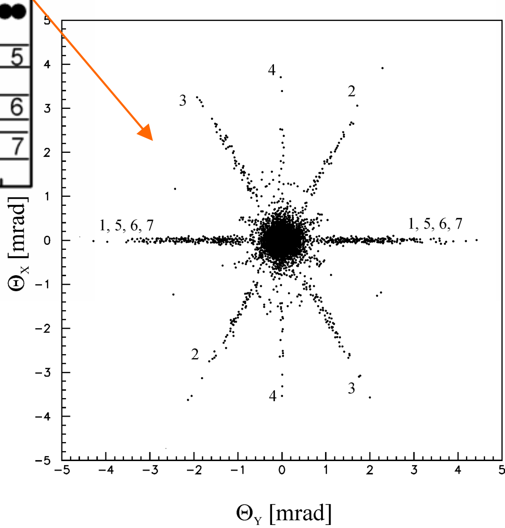
**Proton impact parameters**

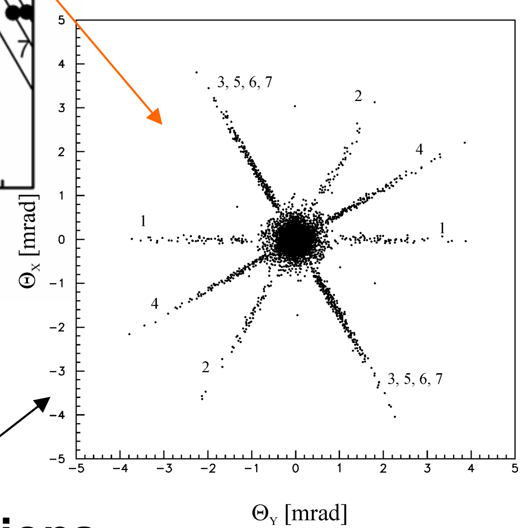



**Relative orientation of nanotubes = π/60**



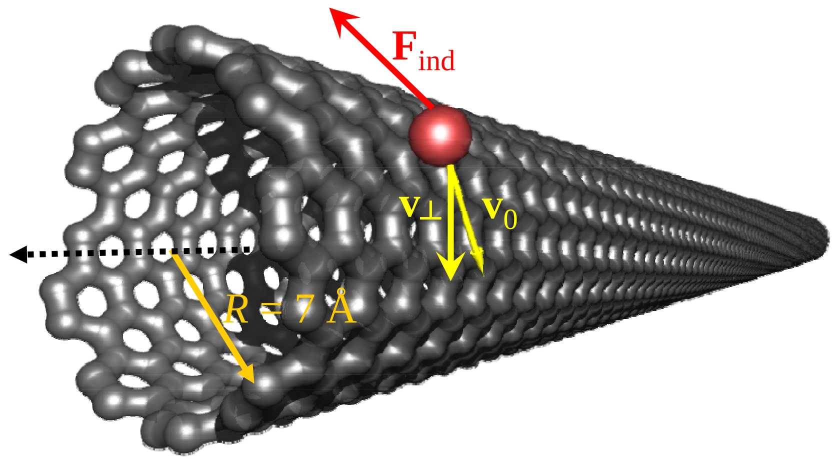

**Rope length 10 μm**



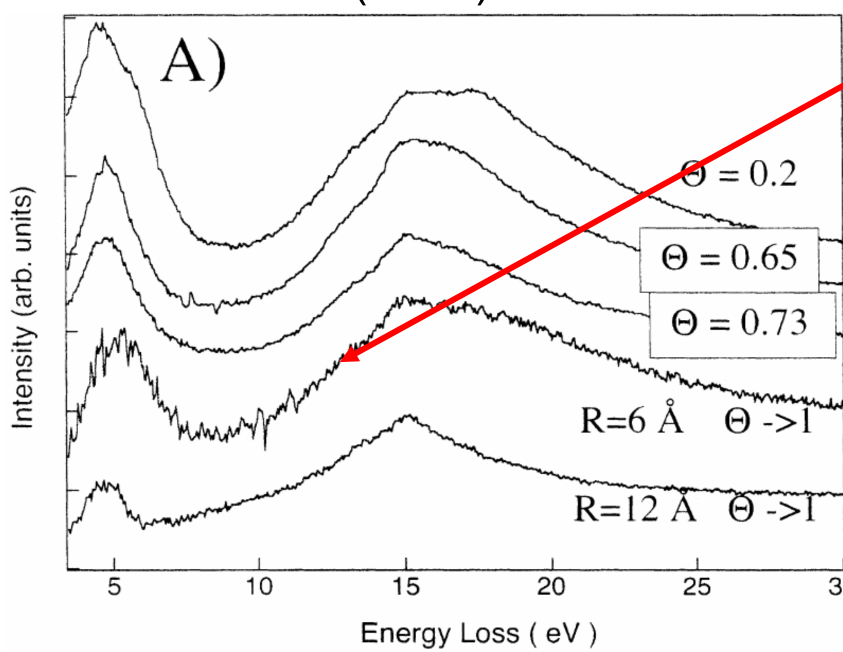



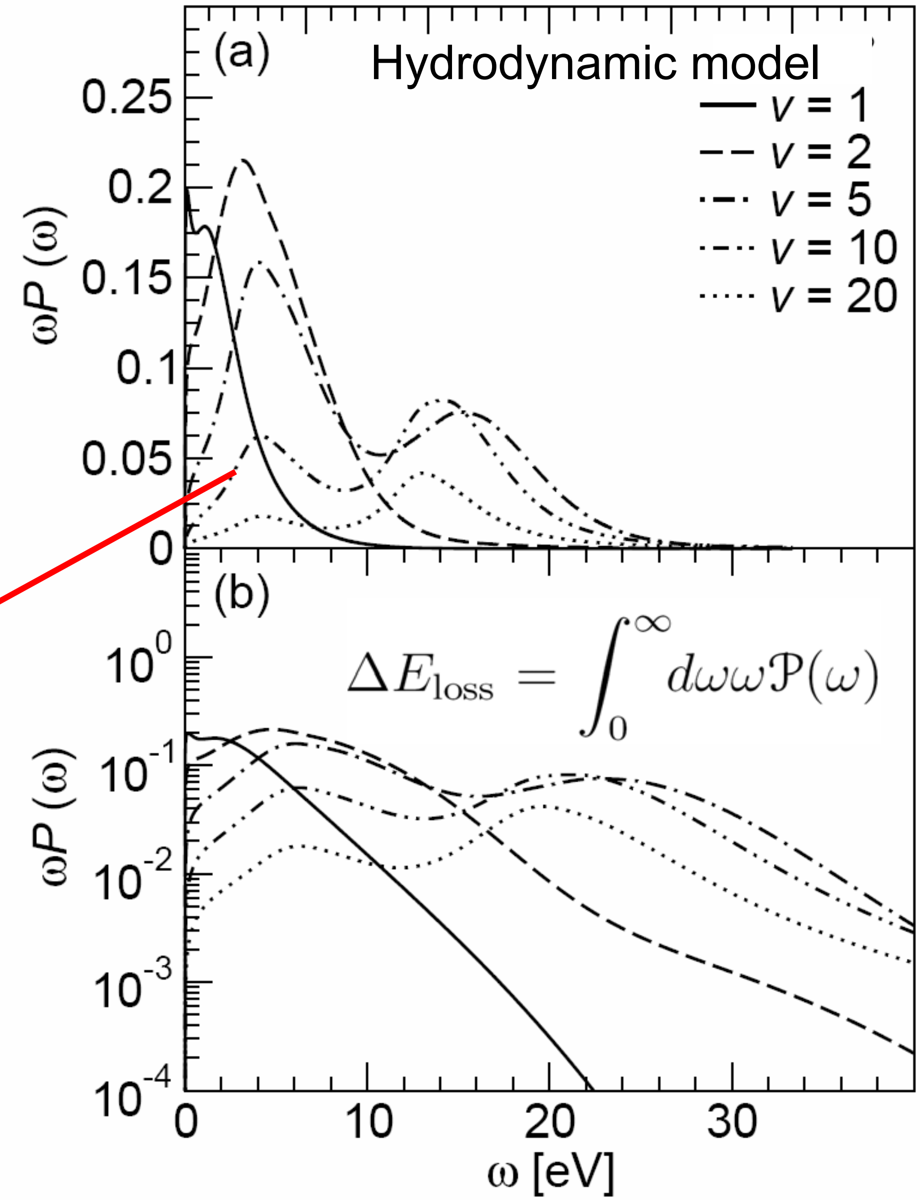

**Angular distributions**

# Energy loss at **oblique** incidence in EELS



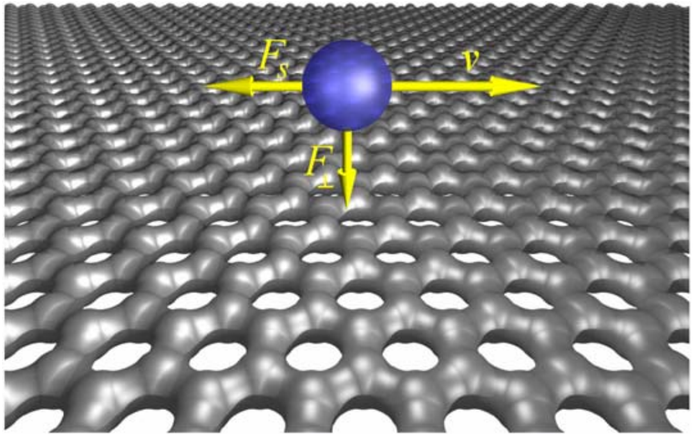

Experiment: O. Stephan *et al., Phys. Rev.* B 66 (2002) 155422



# Grazing scattering of **fast** protons from graphene: 3D

J. Zuloaga *et al.*, *Nucl. Instr. Meth.* B 256 (2007) 162

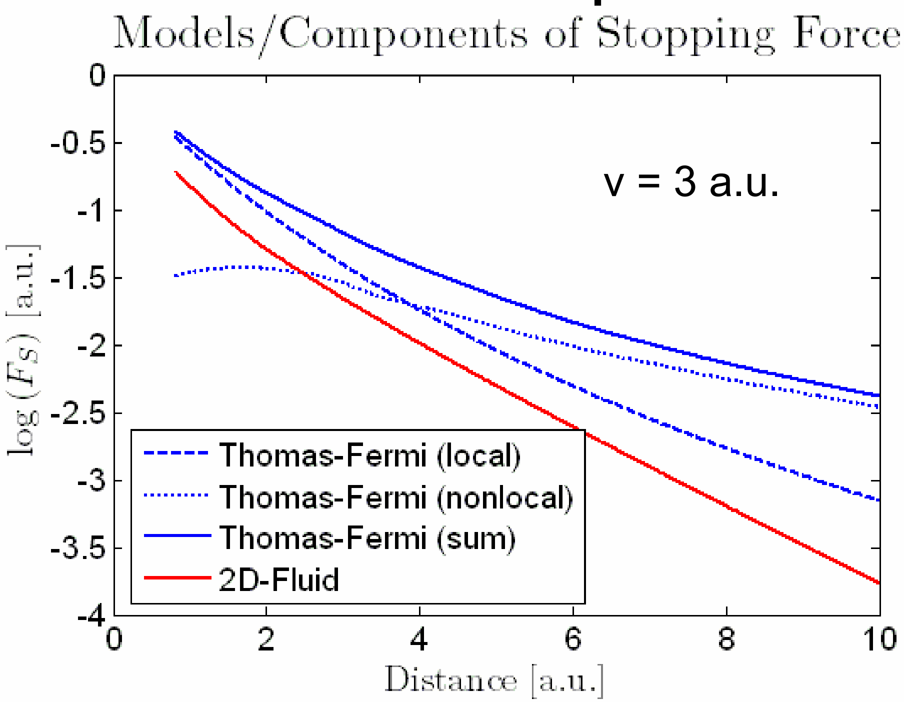


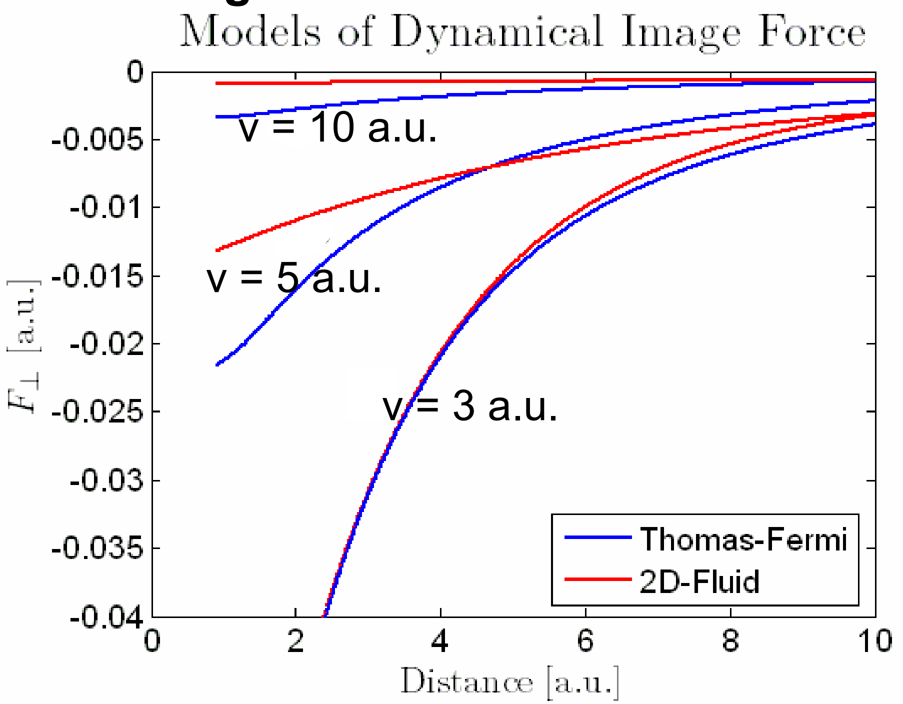

Kitagawa's dielectric function (high-frequency approx.)

$$\epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_2, \omega) \cong \frac{\omega^2}{\omega^2 - \omega_p^2(\mathbf{r}_1)} \left[ \delta(\mathbf{r}_1 - \mathbf{r}_2) - \frac{1}{\omega^2 - \omega_p^2(\mathbf{r}_2)} \frac{(\mathbf{r}_2 - \mathbf{r}_1)}{|\mathbf{r}_2 - \mathbf{r}_1|^3} \cdot \vec{\nabla} n(\mathbf{r}_1) \right]$$

Local + Non-local terms

**Compare 3D and 2D electron-gas models**



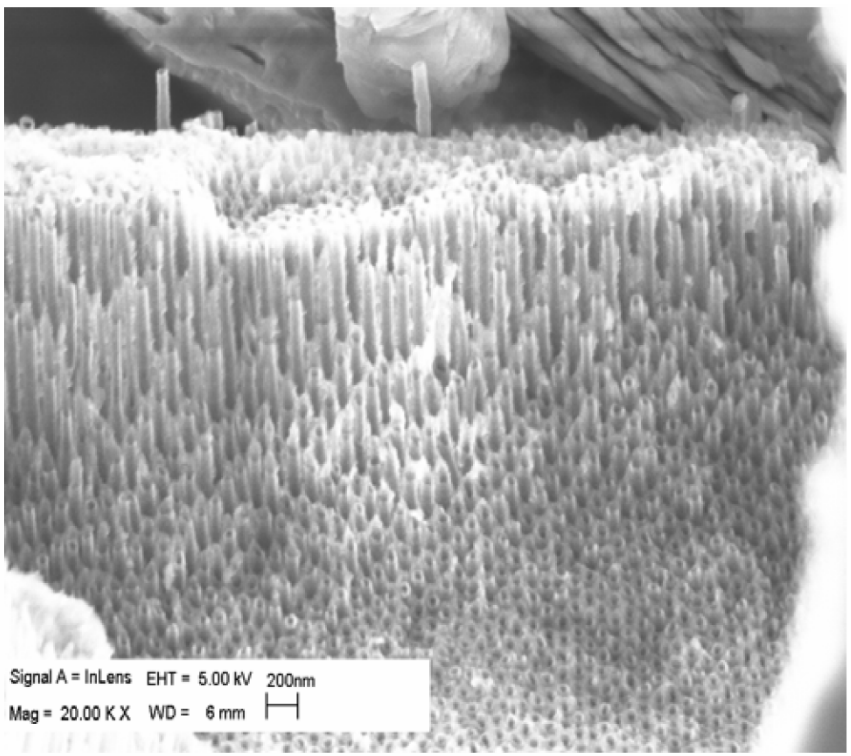



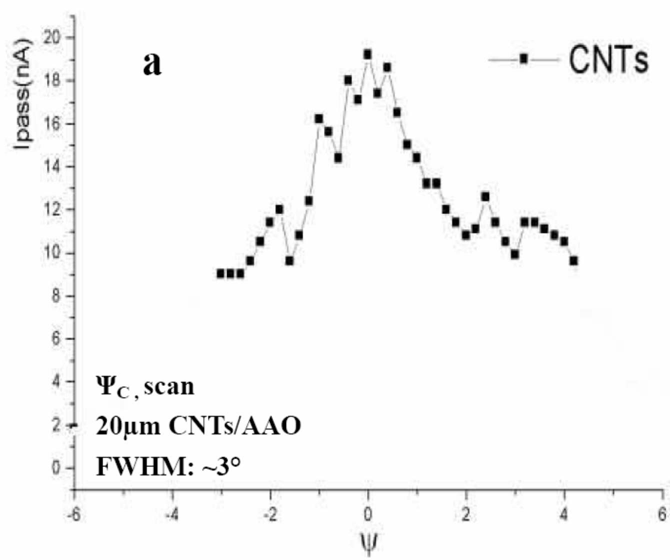
# Actual experimental realization of channelling of 2 MeV $He^+$ ions in MWNTs grown in Anodic Aluminium Oxide

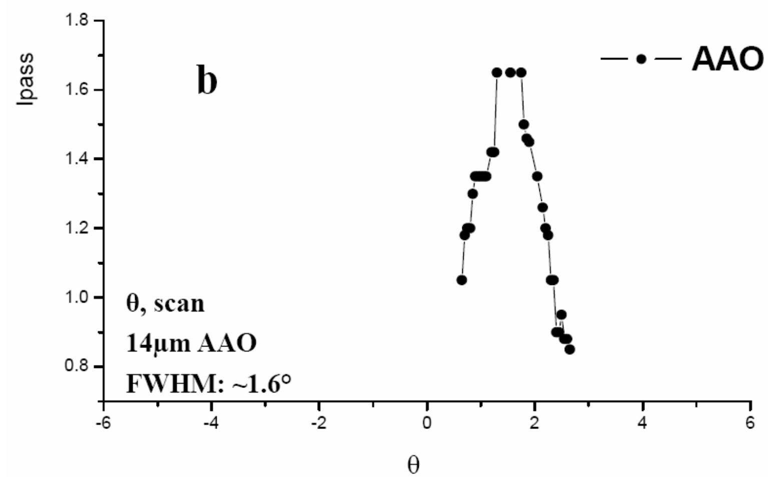
Z. Zhu *et al.*, *Proc. SPIE* 5974 (2005)

Current intensity distributions vs. incidence angles

Side view of AAO membrane

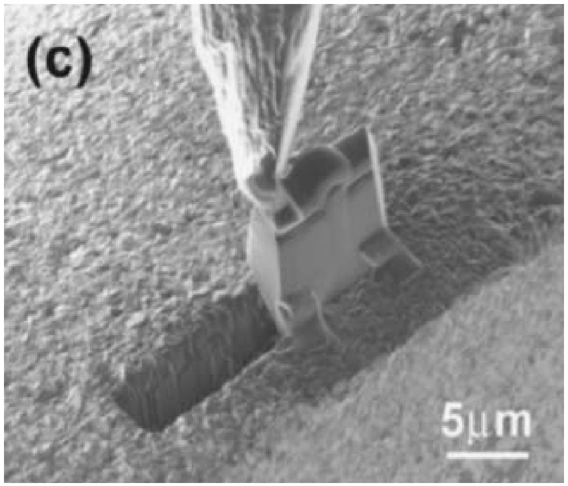


# Electron channelling through a C-fiber coated ~1 µm long MWNT in TEM (electron energy ~300 keV)

G. Chai *et al.*, *Appl. Phys. Lett.* 91 (2007) 103101



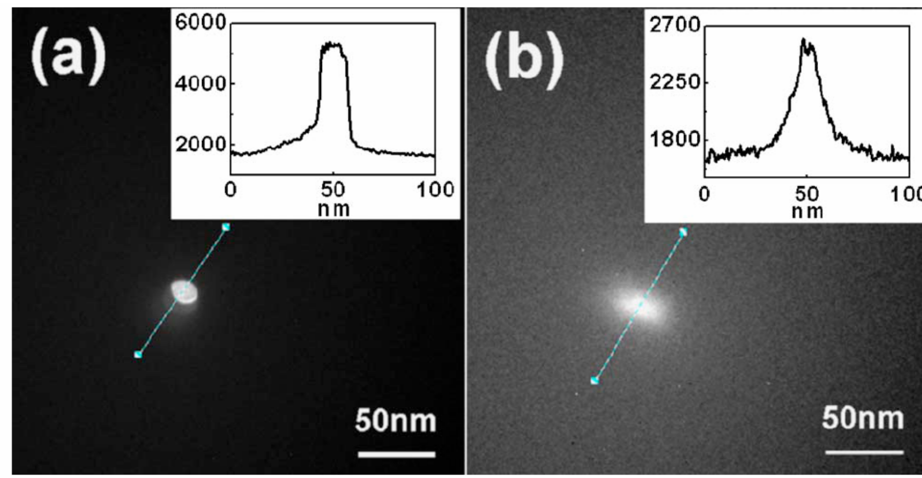




FIG. 4. (Color online) TEM micrographs of a 3 $\mu$m long CNT section under a tilt of 0° (a) and under a tilt of 1° (b). The inserts show the intensity profiles of the transmitted electron beam in the imaging plane along the indicated line scans.

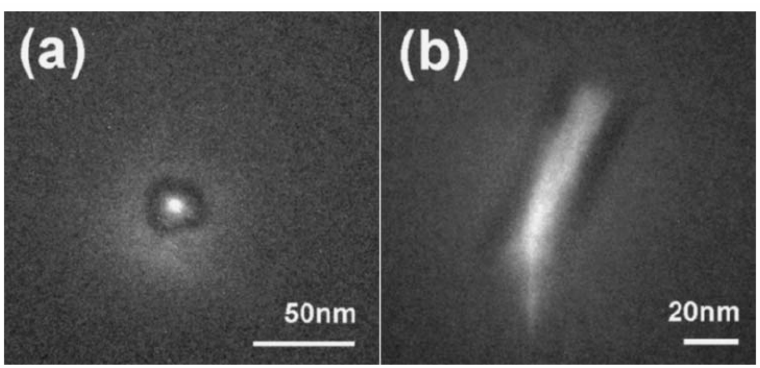
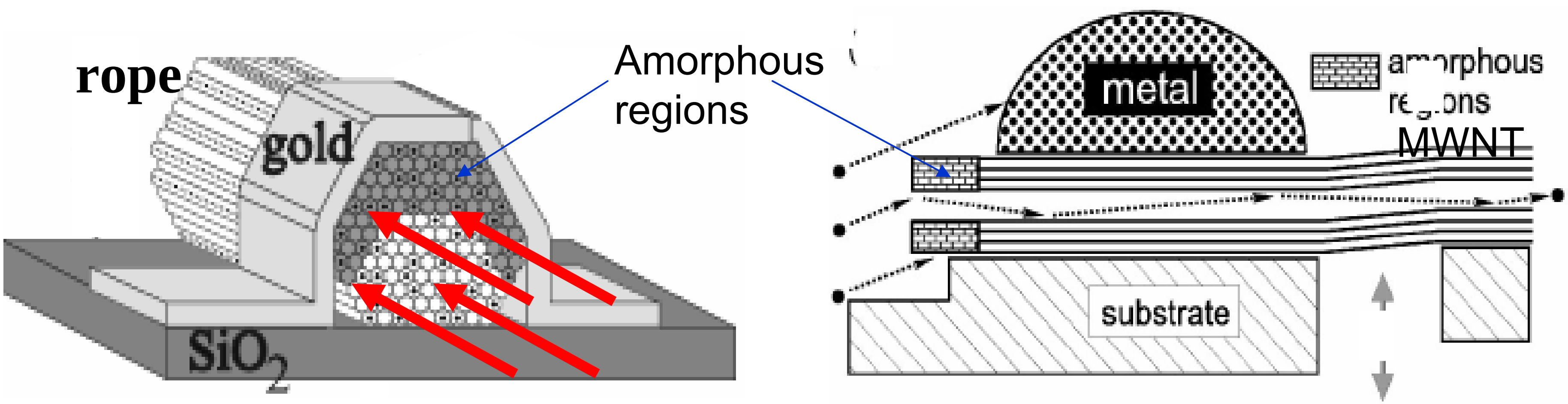



FIG. 3. TEM images of a single CNT section aligned to the electron beam under 0° tilt (a) and under a tilt angle of 5° (b). The image with large tilt angle reveals the inner diameter of the tube of 13 nm.

# Problems: how to open nanotube end & control damage

- Amorphization of open nanotube ends at **low** ion energies
  (A.V. Krasheninnikov and K. Nordlund., *Phys. Rev.* B 71 (2005) 245408).




- At **high** ion energies: amorphization is delayed
  (experiment:100 MeV $Au^+$ ions: A. Misra *et al., Diamond & Rel. Mater*. (2006)).
- Electronic damage still uncertain in channeling (however,
  CNTs are ballistic conductors: *S.* Bellucci, *NIMB* (2005)) .