Electron Energy Loss Spectra of Graphite, Graphene and Carbon Nanotubes: Plasmon Dispersion and Crystal Local Field Effects.

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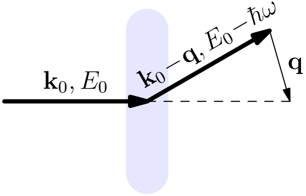
20. 11. 2008 — MORE08 Vienna/Austria

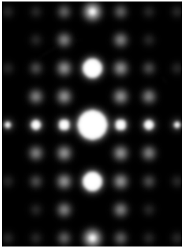
ETSF European Theoretical Spectroscopy Facility — cea — ÉCOLE POLYTECHNIQUE — NanoSciences ILE-DE-FRANCE

What do we want to describe?



collective excitations

- Coulomb interaction
- probed by EELS, IXS



contributions to the spectra

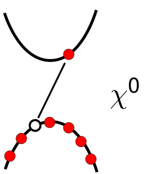
- **elastic scattering** $\rightarrow$ crystal structure
- **inelastic scattering** $\rightarrow$ collective excitations

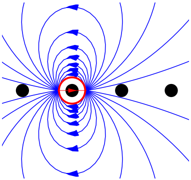
Key quantity: $S(\boldsymbol{q}, \omega) \propto -q^2\, \Im\{\epsilon^{-1}(\boldsymbol{q}, \omega)\}$

How do we calculate ϵ^{-1}?

ab initio calculations

1. ground state calculation gives ϕ_i^{KS}
2. independent-particle polarisability χ^0
3. RPA full polarisability $\chi = \chi^0 + \chi^0 v \chi$
4. dielectric function $\epsilon^{-1} = 1 + v\chi$





(ϵ^{-1}: no retardation, no multiple scattering, no Bragg reflection of the incident electron)

Codes:
ABINIT: X. Gonze *et al.*, Comp. Mat. Sci. **25**, 478 (2002)
DP-code: `www.dp-code.org`; V. Olevano, *et al.*, unpublished.

Self-Consistent Hartree Potentials

long range v_0

- difference between EELS and absorption
- vanishes for large q
- vanishes for localised systems

short range $\bar{v}$

- crystal local field effects in solids
- depolarisation in finite systems

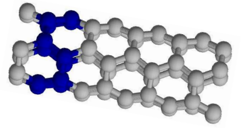
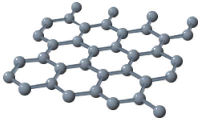
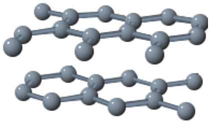
Outlook

dimensionality

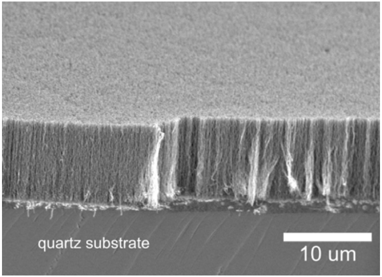
1. induced Hartree potentials in low dimensional systems
   ⇒ linear plasmon dispersion in SWCNT + Graphene
2. assembling nanoobjects
   ⇒ role of interaction

inhomogenitiy

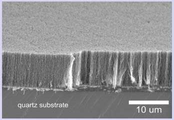
3. crystal local field effects in solids
   ⇒ enhanced anisotropy in Graphite

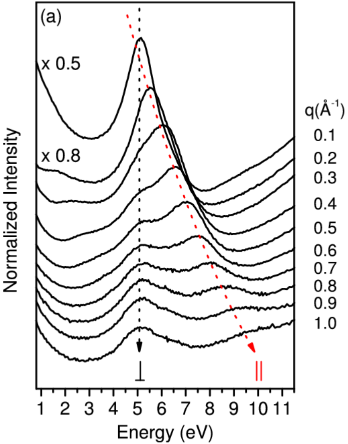
Single-Wall CNT
experiments



Vertical Aligned SWNT



EEL spectra



specimen

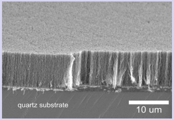
- oriented SWCNT
- diameter: 2 nm
- nearly isolated

spectroscopy

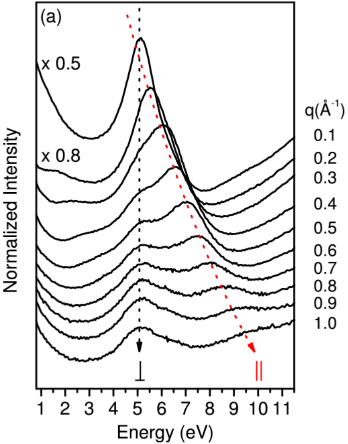
- angular-res. EELS
- resolution:
  $\Delta E = 0.2\,\mathrm{eV}$
  $\Delta q = 0.05$ Å^{-1}

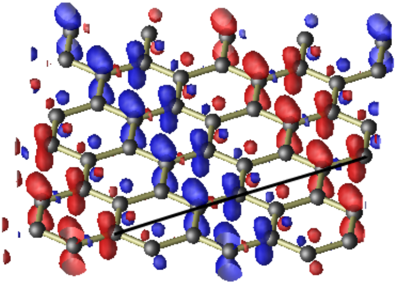
[C. Kramberger, M.Rümmeli, M. Knupfer, J. Fink, B.Büchner, T. Pichler, IFW Dresden, Germany]

Vertical Aligned SWNT



EEL spectra

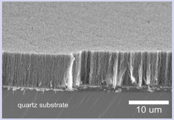




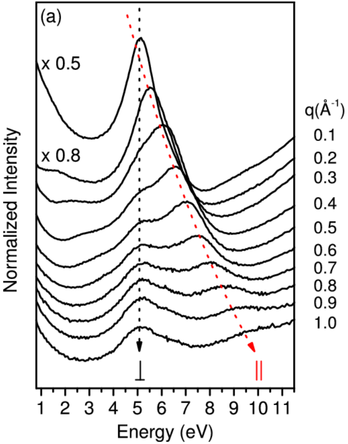
π plasmon at 9eV in Graphite

[C. Kramberger, M.Rümmeli, M. Knupfer, J. Fink, B.Büchner, T. Pichler, IFW Dresden, Germany]

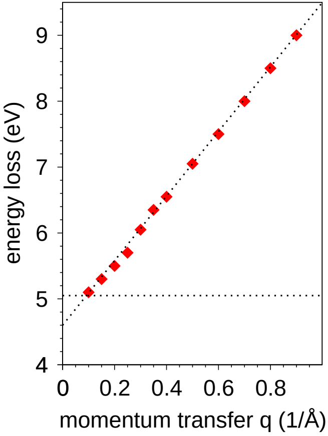
Vertical Aligned SWNT



EEL spectra



(a) Experiment



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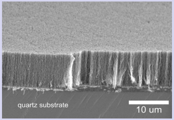
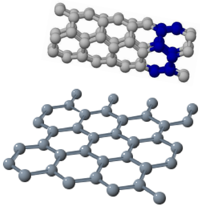
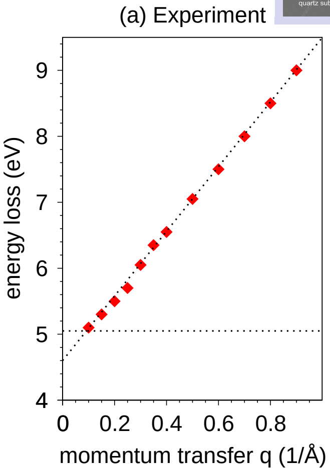
Vertical Aligned SWNT



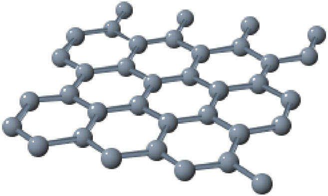
- linear π plasmon dispersion
- SWNT $\Leftrightarrow$ graphene

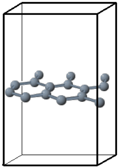




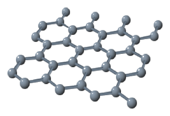
[C. Kramberger, M.Rümmeli, M. Knupfer, J. Fink, B.Büchner, T. Pichler, IFW Dresden, Germany]

Graphene
calculations

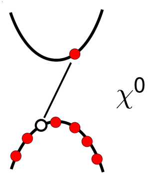




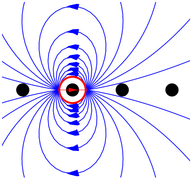
ϵ^{-1} in isolated nanosystems



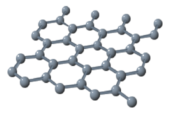
IPA: $\Im\{\epsilon^{-1}\} \propto \Im\{\chi^0\}$
$\rightarrow$ sum of interband transitions



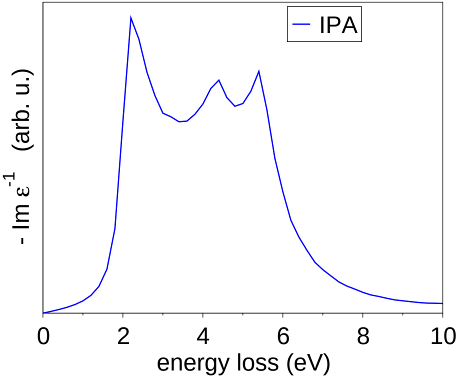
RPA: $\Im\{\epsilon^{-1}\} \propto \Im\{\chi\}$
full susceptibility $\chi = \chi^0(1 - v\chi^0)^{-1}$
contains self-consistent response
$\rightarrow$ mixing of interband transitions



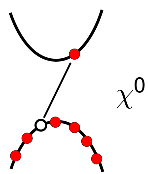
IPA: independent particles



energy loss in graphene
(in-plane, $q = 0.41$ Å^{-1})



$\Longrightarrow$ given by $\Im\{\chi^0\}$:
interpretation in terms of
band-transitions



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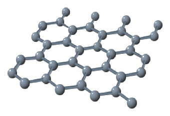

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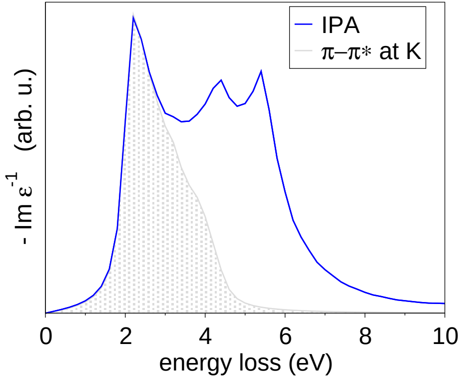
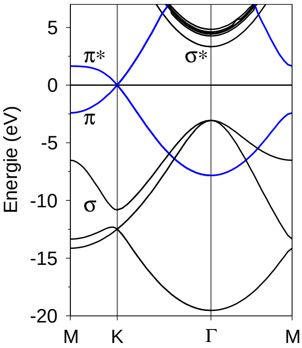
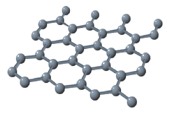


bandstructure



RPA: random phase approximation



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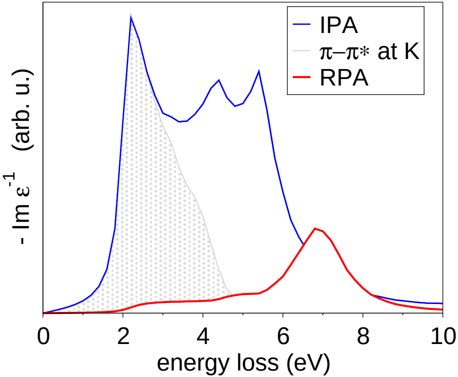
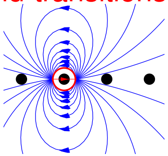
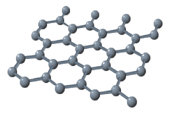


- given by $\Im\{\chi\}$:
  no interpretation by
  ~~band-transitions~~



- contributions from K
- mixing of dispersion

RPA: random phase approximation



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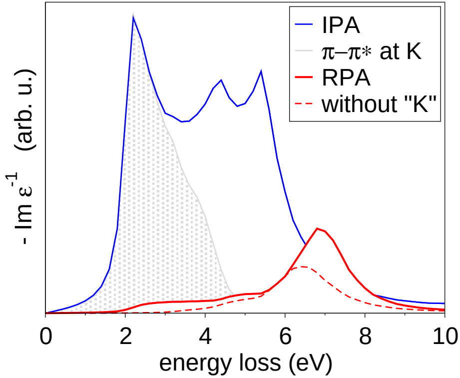

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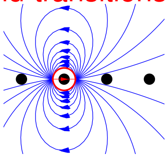
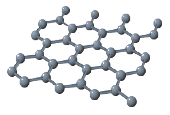
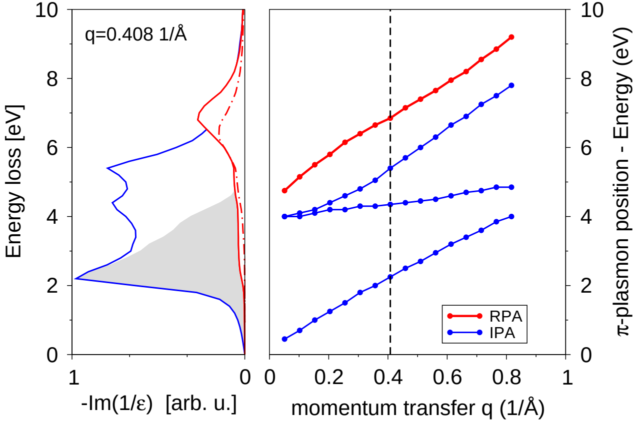


- contributions from K
- mixing of dispersion

Plasmon dispersion

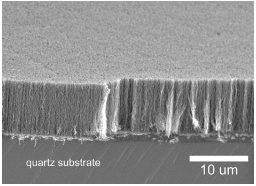


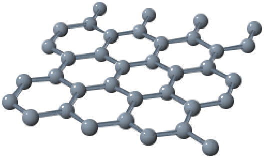


[1] P. Longe, and S. M. Bose, Phys. Rev. B **48**, 18239 (1993)
[2] F. L. Shyu and M. F. Lin, Phys. Rev. B **62**,8508 (2000)

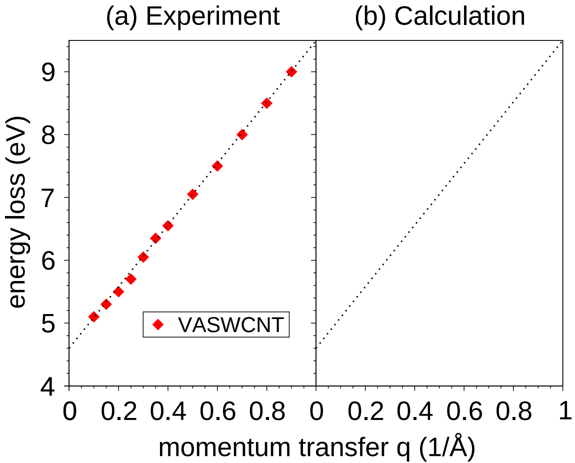
SWNT vs. Graphene

comparison





SWCNT vs. Graphene



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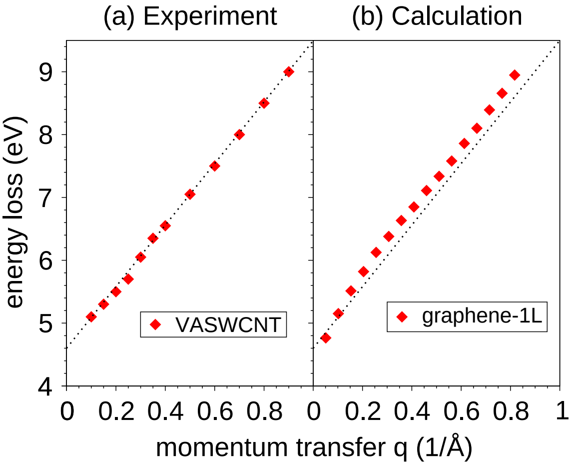
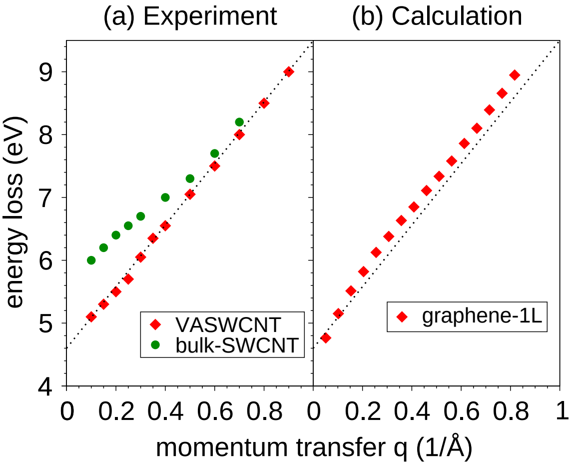
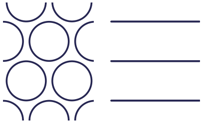


Role of Interactions





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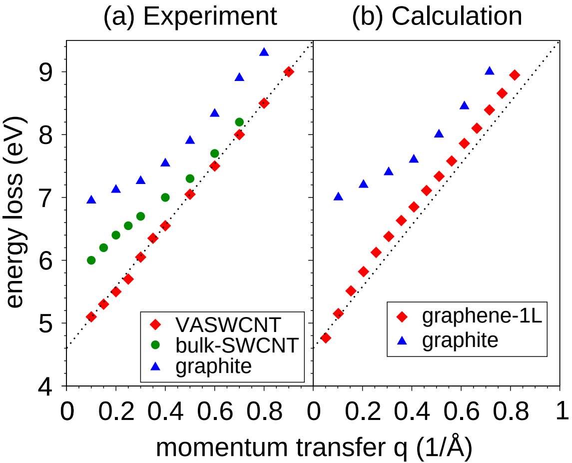

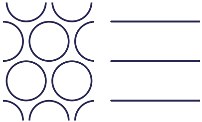

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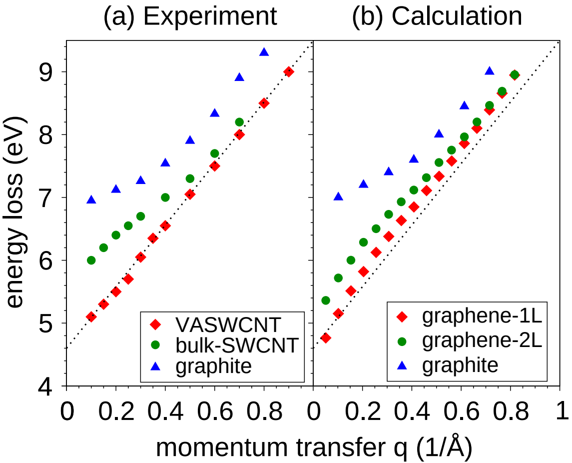
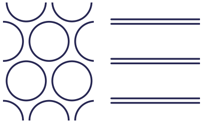
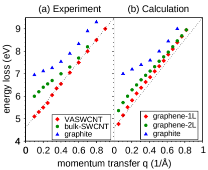




Conclusions

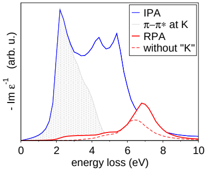
SWCNT $\Longleftrightarrow$ graphene

- isolated SWCNT $\Longleftrightarrow$ graphene-1L
- bundled SWCNT $\Longleftrightarrow$ graphene-2L



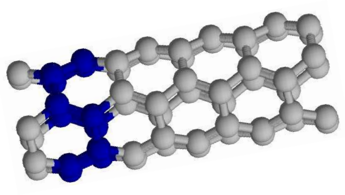
graphene

- induced Hartree potentials important
- ~~picture of independent transitions~~
- mixing of transitions/dispersions
  $\rightarrow$ leads to linear dispersion

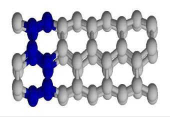


Single-Wall CNT

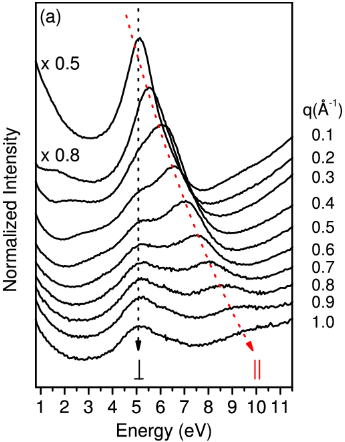
calculations [Xochitl Lopez]



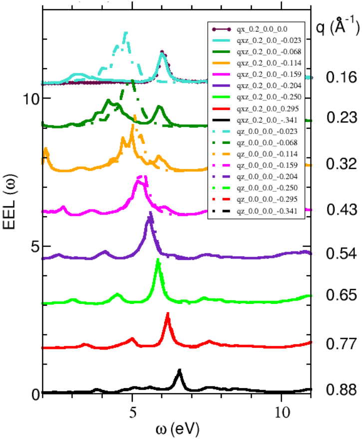
(3,3) Single Wall Carbon nanotube



Experiment: oriented SWCNT
(Diameter 20 Å, nearly isolated)



Calculation: (3,3) SWCNT
(Diameter 4 Å, low interaction)

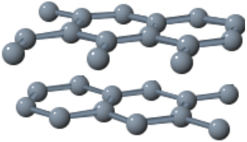


Graphite

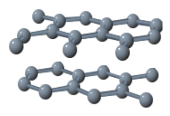
calculation: revealing an angular anomaly

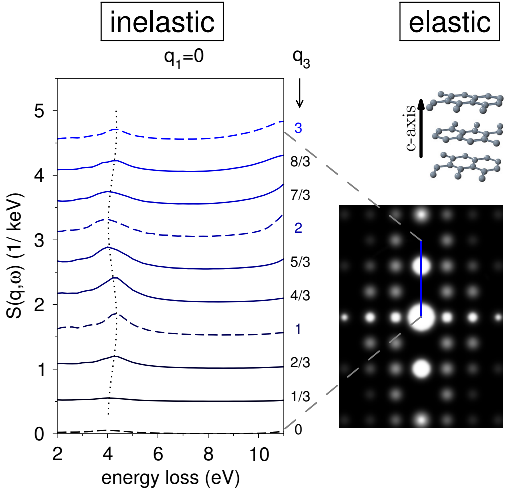
explication: in terms of crystal local field effects

experiment: verification by inelastic x-ray scattering



On-axis: continuous

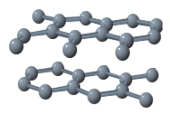


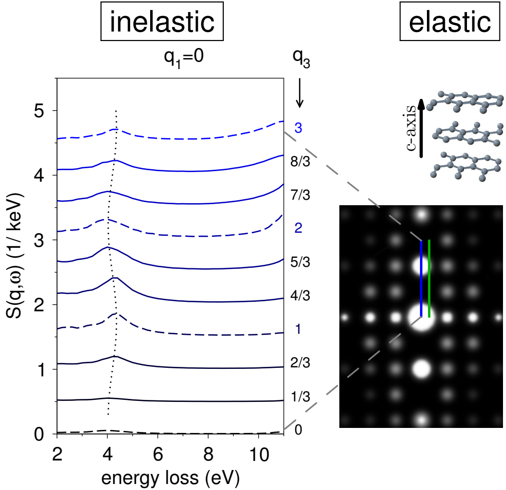


- energy loss $S(\boldsymbol{q}, \omega)$ in graphite (AB)
- $\boldsymbol{q}$ along c-axis
- weak dispersion[1]
- and off-axis?

[1] Y. Q. Cai *et. al.*, Phys. Rev. Lett. **97**, 176402 (2006)

On-axis: continuous





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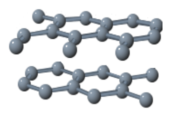
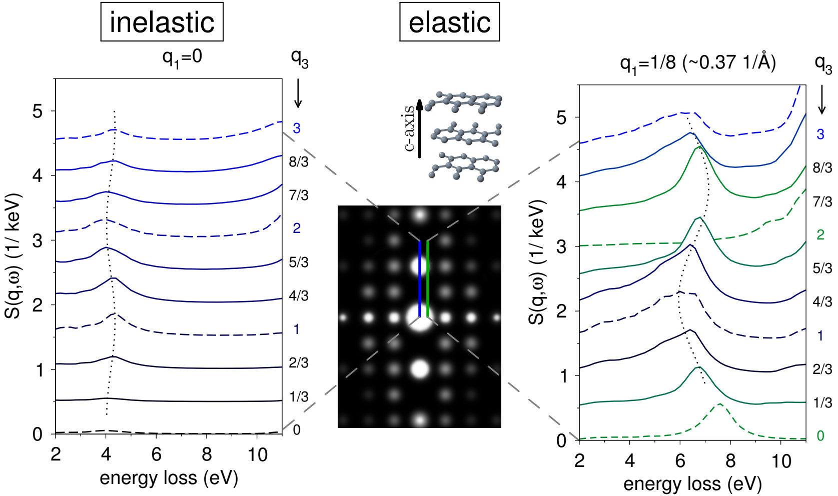
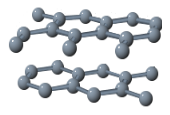
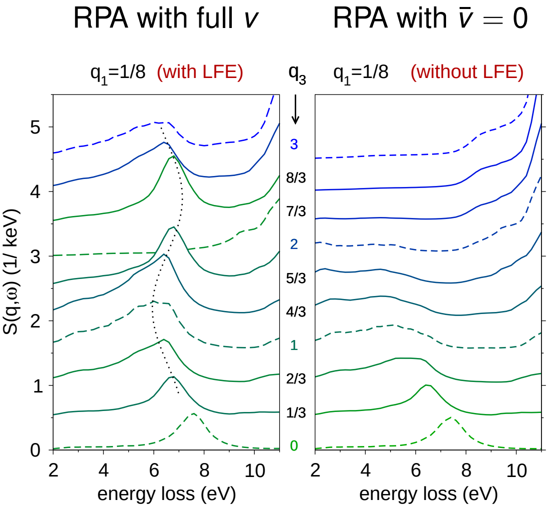
Off-axis: discontinuous!



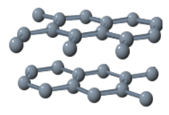


What is the origin?



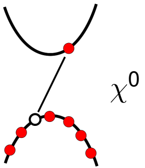


Crystal Local Field Effects



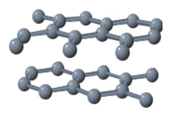
dielectric function in crystals

- recall: $\epsilon^{-1} = 1 + v\chi, \quad \chi = \chi^0 + \chi^0 v \chi$
- RPA: $\epsilon = 1 - v\chi^0$
- ϵ is a matrix: $\epsilon(\boldsymbol{q}, \boldsymbol{q}'; \omega) = \left(\epsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}_r, \omega)\right)$
- energy loss function (EELS, IXS)
  $S(\boldsymbol{q}, \omega) \propto -\Im\{\epsilon^{-1}_{\boldsymbol{G}\boldsymbol{G}}(\boldsymbol{q}_r, \omega)\}, \quad \boldsymbol{q} = \boldsymbol{q}_r + \boldsymbol{G}$



$\Rightarrow$ mixing of all transitions in χ^0
$\Rightarrow$ crystal local field effects (LFE)

Physical picture of LFE: Dipoles



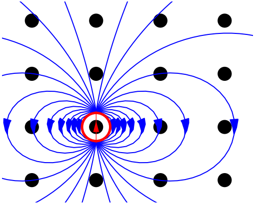
Two ways of understanding crystal local field effects:

dipole picture

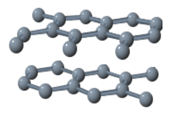
perturbation — induced dipoles

$$\varphi^t \underset{\cdots\cdots\cdots}{\overset{\text{sc}}{\rightleftarrows}} \varphi^i$$

- induced local fields
- crystal structure important



Physical picture of LFE: Coupled modes



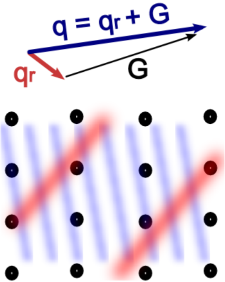
plane wave picture

perturbing mode — induced mode

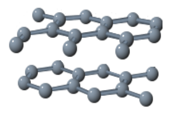
$$e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \underset{\text{sc}}{\rightleftarrows} e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

- Bragg-reflection inside the crystal
- couples modes with same $\boldsymbol{q}_r$
- $\epsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}_r)$ describes coupling $\frac{\delta\varphi^i(\boldsymbol{G})}{\delta\varphi^t(\boldsymbol{G}')}$

$\Rightarrow$ *key for understanding the discontinuity*



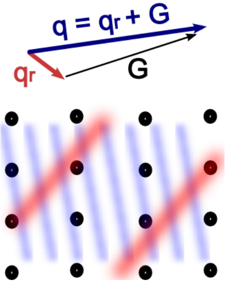
Simple 2×2 model for LFE



- dominant coupling between the two modes $\mathbf{0}$ and $\boldsymbol{G} = (0,0,2)$

$$\begin{pmatrix} \epsilon_{\mathbf{00}} & \cdots & \epsilon_{\mathbf{0}\boldsymbol{G}} & \cdots \\ \vdots & & \vdots & \\ \epsilon_{\boldsymbol{G}\mathbf{0}} & \cdots & \epsilon_{\boldsymbol{GG}} & \cdots \\ \vdots & & \vdots & \end{pmatrix} \longrightarrow \begin{pmatrix} \epsilon_{\mathbf{00}} & \epsilon_{\mathbf{0}\boldsymbol{G}} \\ \epsilon_{\boldsymbol{G}\mathbf{0}} & \epsilon_{\boldsymbol{GG}} \end{pmatrix}$$

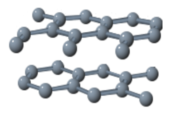
we introduce an effective 2×2-matrix $\tilde{\epsilon}$



- Remember: the loss function was

$$S(\boldsymbol{q},\omega) \propto -\Im\{\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega)\}$$

Simple 2 × 2 model for LFE

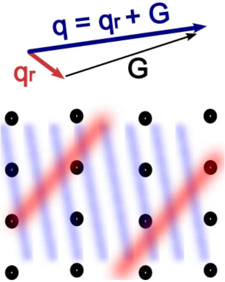


- inverting the effective 2 × 2-matrix $\tilde\epsilon$

$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde\epsilon_{\boldsymbol{GG}}} + \frac{\tilde\epsilon_{\boldsymbol{G0}}\tilde\epsilon_{\boldsymbol{0G}}}{(\tilde\epsilon_{\boldsymbol{GG}})^2}\;\epsilon^{-1}_{\mathbf{00}}(\boldsymbol{q}_r,\omega)$$

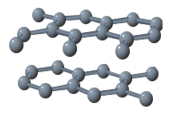
without LF correction ...

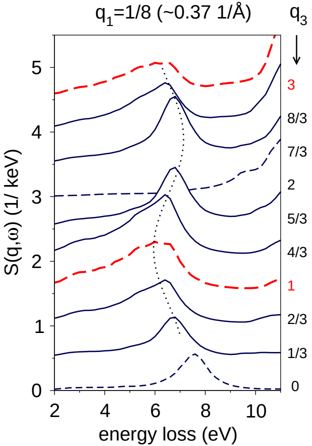
(known as *two plasmon-band model*[2])



[2] L. E. Oliveira, K. Sturm, Phys. Rev. B **22**, 6283 (1980).

1. Recurring excitations





$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde{\epsilon}_{\boldsymbol{GG}}} + \frac{\tilde{\epsilon}_{\boldsymbol{G0}}\tilde{\epsilon}_{\boldsymbol{0G}}}{(\tilde{\epsilon}_{\boldsymbol{GG}})^2}\ \epsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q}_r,\omega)$$

$$S(\boldsymbol{q}_r+\boldsymbol{G}) = S^{\text{NLF}}(\boldsymbol{q}_r+\boldsymbol{G}) + f\cdot S(\boldsymbol{q}_r)$$

coupling of excitations of momentum

$\boldsymbol{q}_r$ 1. Brillouin zone

$\boldsymbol{q}_r+\boldsymbol{G}$ higher Brillouin zone

$\Rightarrow$ reappearance[3] of the anisotropic spectra from $\boldsymbol{q}\to\boldsymbol{0}$

[3] K. Sturm, W. Schülke, J. R. Schmitz, Phys. Rev. Lett. **68**, 228 (1992).

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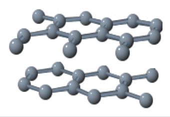

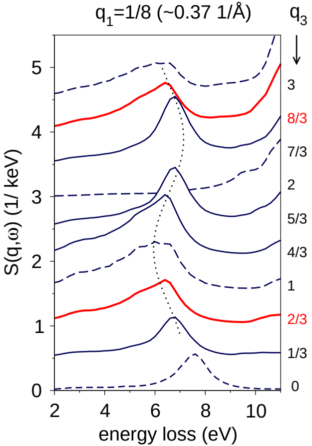

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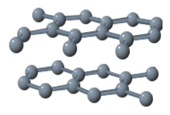

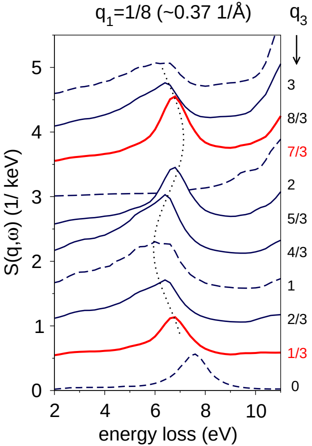

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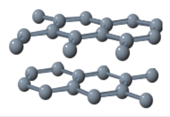
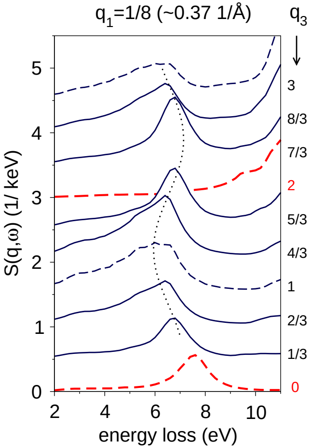
2. Strength of coupling



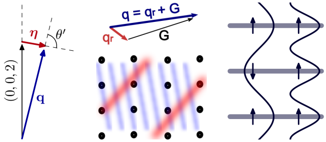


$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde{\epsilon}_{\boldsymbol{GG}}} + \frac{\tilde{\epsilon}_{\boldsymbol{G0}}\tilde{\epsilon}_{\boldsymbol{0G}}}{(\tilde{\epsilon}_{\boldsymbol{GG}})^2}\ \epsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q}_r,\omega)$$

strength of coupling $\epsilon_{\boldsymbol{G0}}$ depends on:

- angle $\angle(\boldsymbol{q}_r, \boldsymbol{q}_r + \boldsymbol{G})$ and
- structure factor $\propto$ density $n_{\boldsymbol{G}}$

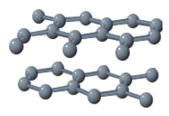
$\Rightarrow$ enhances the angular anomaly

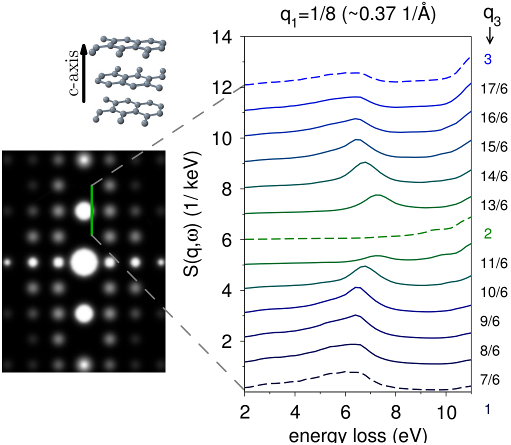


Experimental verification

by inelastic x-ray scattering

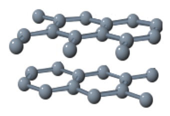
IXS experiments

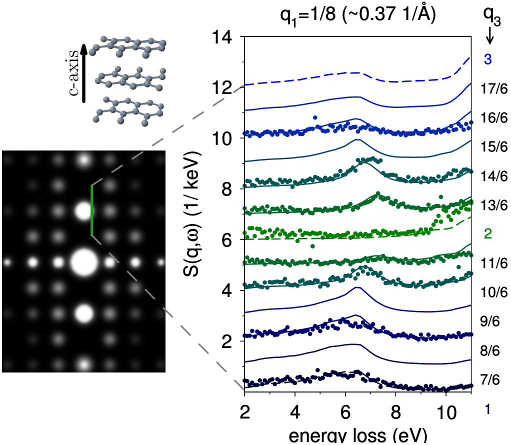




- IXS experiments
  N. Hiraoka
  (Spring8, Taiwan)
- elastic tail removed
- uniform scaling

IXS experiments





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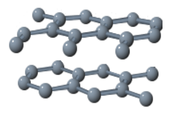
Conclusions



graphite

- angular anomaly close to Bragg reflections
- originates from local field effects (coupling to 1. BZ):
  1. spectrum from $\boldsymbol{q} \to 0$ reappears (direction of $\boldsymbol{q}_r$)
  2. coupling $\epsilon_{\boldsymbol{G}\boldsymbol{0}}(\boldsymbol{q}_r)$ enforces anisotropy

other systems

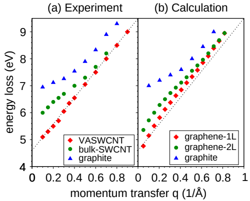
- *all* systems with strong local field effects
  e. g. layered systems, 1D structures

$\Rightarrow$ caution with loss experiments close to Bragg reflections

Summary

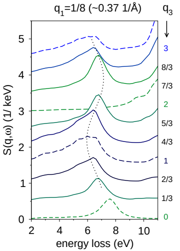
dimensionality

1. strong mixing of transitions (large energy range) in low dimensional systems (→ linear plasmon dispersion)
2. interactions important for small $\boldsymbol{q}$



inhomogenity

3. discontinouity in $S(\boldsymbol{q}, \omega)$ close to Bragg reflections (result of plasmon bands)



Thank you for your attention!

publications:

Linear Plasmon Dispersion in Single-Wall Carbon Nanotubes and the Collective Excitation Spectrum of Graphene

C. Kramberger, R. H., C. Giorgetti, M. Rümmeli, M. Knupfer, J. Fink, B. Büchner, Lucia Reining, E. Einarsson, S. Maruyama, F. Sottile, K. Hannewald, V. Olevano, A. G. Marinopoulos, and T. Pichler

[Phys. Rev. Lett. **100**, 196803 (2008)]

Anomalous Angular Dependence of the Dynamic Structure Factor near Bragg Reflections: Graphite

R. H., C. Giorgetti, N. Hiraoka, Y. Q. Cai, F. Sottile, A. G. Marinopoulos, F. Bechstedt, and Lucia Reining

[accepted by Phys. Rev. Lett. (2008)]

codes:

ABINIT: X. Gonze *et al.*, Comp. Mat. Sci. **25**, 478 (2002)

DP-code: `www.dp-code.org`; V. Olevano, *et al.*, unpublished.