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What do we want to describe?

Collective excitations

- Coulomb interaction
- Probed by EELS, IXS

Contributions to the spectra

- **Elastic scattering** → crystal structure
- **Inelastic scattering** → collective excitations

Key quantity: \( S(q, \omega) \propto -q^2 \Im\{\epsilon^{-1}(q, \omega)\} \)
How do we calculate $\epsilon^{-1}$?

**ab initio calculations**

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

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

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

inhomogenity

3. crystal local field effects in solids
   ⇒ enhanced anisotropy in Graphite
Single-Wall CNT experiments
EEL spectra

specimen

- oriented SWCNT
- diameter: 2 nm
- nearly isolated

spectroscopy

- angular-res. EELS
- resolution:
  \[ \Delta E = 0.2 \text{ eV} \]
  \[ \Delta q = 0.05 \text{ Å}^{-1} \]

[ 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]
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Vertical Aligned SWNT

- linear $\pi$ plasmon dispersion
- SWNT $\leftrightarrow$ graphene

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

(a) Experiment

<table>
<thead>
<tr>
<th>$q$ (1/Å)</th>
<th>Energy loss (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>0.4</td>
<td>6</td>
</tr>
<tr>
<td>0.6</td>
<td>7</td>
</tr>
<tr>
<td>0.8</td>
<td>8</td>
</tr>
<tr>
<td>1.0</td>
<td>9</td>
</tr>
</tbody>
</table>

Energy loss versus momentum transfer $q$ (1/Å)
Graphene calculations
\(\frac{1}{\epsilon - 1}\) in isolated nanosystems

**IPA:** \(\Im \{\frac{1}{\epsilon - 1}\} \propto \Im \{\chi^0\}\)

\(\rightarrow\) sum of interband transitions

**RPA:** \(\Im \{\frac{1}{\epsilon - 1}\} \propto \Im \{\chi\}\)

Full susceptibility \(\chi = \chi^0(1 - \nu\chi^0)^{-1}\)

contains self-consistent response

\(\rightarrow\) mixing of interband transitions
IPA: independent particles

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

\[ \text{IPA} \]

\[ \implies \text{given by } \Im \{ \chi^0 \} : \]
interpretation in terms of band-transitions

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Collective Excitations in Carbon Systems
ipa: independent particles

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

- \( \text{Im} \, \epsilon^{-1} \) (arb. u.)

energy loss (eV)

bandstructure

- \( \pi^* \)
- \( \pi \)
- \( \sigma^* \)
- \( \sigma \)

Energie (eV)

-20 -15 -10 -5 0 5
RPA: random phase approximation

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

\[ \text{IPA}\]
\[ \pi-\pi^* \text{ at K} \]
\[ \text{RPA} \]

- \( \text{Im} \varepsilon^{-1} \) (arb. u.)
- energy loss (eV)

- given by \( \Im\{\chi\} \): no interpretation by band-transitions
- contributions from K
- mixing of dispersion

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RPA: random phase approximation

diagram showing energy loss in graphene (in-plane, $q = 0.41 \text{ Å}^{-1}$).

- Im $\varepsilon^{-1}$ (arb. u.)

- Energy loss (eV)

- IPA
- $\pi-\pi^*$ at K
- RPA
- without "K"

- Contributions from K
- Mixing of dispersion

Given by $\Im\{\chi\}$:
no interpretation by band-transitions.
Plasmon dispersion

SWNT vs. Graphene

comparison
SWCNT vs. Graphene

(a) Experiment
(b) Calculation

energy loss (eV)
momentum transfer q (1/Å)

VASWCNT

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SWCNT vs. Graphene

(a) Experiment
(b) Calculation

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Role of Interactions

(a) Experiment

(b) Calculation

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Role of Interactions

(a) Experiment

(b) Calculation

- VASWCNT
- bulk-SWCNT
- graphite
- graphene-1L
- graphite

momentum transfer $q$ (1/Å)

energy loss (eV)

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Role of Interactions

(a) Experiment
(b) Calculation

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Conclusions

SWCNT ⇔ graphene

- isolated SWCNT ⇔ graphene-1L
- bundled SWCNT ⇔ graphene-2L

graphene

- induced Hartree potentials important
- picture of independent transitions
- mixing of transitions/dispersions → 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

- Inelastic
- Elastic

Energy loss (eV)

$S(q, \omega)$ (1/keV)

$q_1 = 0$

$q_3$

$\text{c-axis}$

- Energy loss $S(q, \omega)$ in graphite (AB)
- $q$ along c-axis
- Weak dispersion
- and off-axis?

On-axis: continuous

- inelastic
  - $q_1=0$
  - $q_3$

- elastic

Energy loss $S(q,\omega)$ in graphite (AB)

- $q$ along c-axis
- weak dispersion
- and off-axis?

Off-axis: discontinuous!

**Inelastic**

$q_1 = 0$

**Elastic**

$q_1 = 1/8 (~0.37 \ 1/\AA)$

$S(q, \omega) \ (1/\text{keV})$

- $3$
- $8/3$
- $7/3$
- $2$
- $5/3$
- $4/3$
- $1$
- $2/3$
- $1/3$
- $0$

Energy loss (eV)

$0$

$1$

$2$

$3$

$4$

$5$
What is the origin?

RPA with full $\nu$

RPA with $\bar{\nu} = 0$

$q_1=1/8$ (with LFE)

$q_3$

$q_1=1/8$ (without LFE)

$S(q, \omega) (1/\text{keV})$

energy loss (eV)

energy loss (eV)
dielectric function in crystals

- recall: $\epsilon^{-1} = 1 + \nu \chi$, $\chi = \chi^0 + \chi^0 \nu \chi$
- RPA: $\epsilon = 1 - \nu \chi^0$
- $\epsilon$ is a matrix: $\epsilon(q, q'; \omega) = (\epsilon_{GG'}(q_r, \omega))$
- energy loss function (EELS, IXS)
  $S(q, \omega) \propto -\Im\{\epsilon^{-1}_{GG}(q_r, \omega)\}$, $q = q_r + G$

⇒ mixing of all transitions in $\chi^0$
⇒ crystal local field effects (LFE)
Two ways of understanding crystal local field effects:

**dipole picture**
- perturbation → induced dipoles
- induced local fields
- crystal structure important
Physical picture of LFE: Coupled modes

- **Plane wave picture**
- **Perturbing mode** induces **induced mode**

\[ e^{i\mathbf{q} \cdot \mathbf{r}} \xrightarrow{\text{sc}} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} \]

- Bragg-reflection inside the crystal
- Couples modes with same \( q_r \)
- \( \epsilon_{GG'}(q_r) \) describes coupling \( \frac{\delta \varphi^i(G)}{\delta \varphi^t(G')} \)

\[ \Rightarrow \text{key for understanding the discontinuity} \]
Simple $2 \times 2$ model for LFE

- dominant coupling between the two modes $0$ and $G = (0, 0, 2)$

$$
\begin{pmatrix}
\epsilon_{00} & \ldots & \epsilon_{0G} & \ldots \\
\vdots & & \vdots & \\
\epsilon_{G0} & \ldots & \epsilon_{GG} & \ldots \\
\vdots & & \vdots & \\
\end{pmatrix}
\longrightarrow
\begin{pmatrix}
\epsilon_{00} & \epsilon_{0G} \\
\epsilon_{G0} & \epsilon_{GG} \\
\end{pmatrix}
$$

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

- Remember: the loss function was

$$
S(q, \omega) \propto -\Im\{\epsilon_{GG}^{-1}(q_r, \omega)\}
$$
Simple $2 \times 2$ model for LFE

inverting the effective $2 \times 2$-matrix $\tilde{\epsilon}$

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

without LF correction ...

(known as *two plasmon-band model*\(^2\))

1. Recurring excitations

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

$$S(q_r + G) = S^{NLF}(q_r + G) + f \cdot S(q_r)$$

coupling of excitations of momentum

$q_r$ 1. Brillouin zone

$q_r + G$ higher Brillouin zone

$\Rightarrow$ reappearance$^3$ of the anisotropic spectra from $q \rightarrow 0$

1. Recurring excitations

\[ \epsilon^{-1}_{GG}(q_r, \omega) = \frac{1}{\epsilon_{GG}} + \frac{\epsilon_{0G} \epsilon_{0G}}{\epsilon_{GG}} \epsilon^{-1}_{00}(q_r, \omega) \]

\[ S(q_r + G) = S^{\text{NLF}}(q_r + G) + f \cdot S(q_r) \]

coupling of excitations of momentum

\[ q_r \quad 1. \text{Brillouin zone} \]

\[ q_r + G \quad \text{higher Brillouin zone} \]

\[ \Rightarrow \text{reappearance}\textsuperscript{3} \] of the anisotropic spectra from \( q \to 0 \)

\[ ^3\text{K. Sturm, W. Schülke, J. R. Schmitz, Phys. Rev. Lett. 68, 228 (1992).} \]
1. Recurring excitations

$$\epsilon^{-1}_{GG}(q_r, \omega) = \frac{1}{\tilde{\epsilon}_{GG}} + \frac{\tilde{\epsilon}_{G0} \tilde{\epsilon}_{0G}}{\left(\tilde{\epsilon}_{GG}\right)^2} \epsilon^{-1}_{00}(q_r, \omega)$$

$$S(q_r + G) = S^{NLF}(q_r + G) + f \cdot S(q_r)$$

coupling of excitations of momentum

$q_r$ 1. Brillouin zone

$q_r + G$ higher Brillouin zone

$\Rightarrow$ reappearance of the anisotropic spectra from $q \rightarrow 0$

---

2. Strength of coupling

\[ \epsilon_{GG}^{-1}(q_r, \omega) = \frac{1}{\tilde{\epsilon}_{GG}} + \frac{\tilde{\epsilon}_{G0}\tilde{\epsilon}_{0G}}{(\tilde{\epsilon}_{GG})^2} \epsilon_{00}^{-1}(q_r, \omega) \]

**strength of coupling** \( \epsilon_{G0} \) depends on:

- angle \( \angle(q_r, q_r + G) \) and
- structure factor \( \propto \) density \( n_G \)

\( \Rightarrow \) enhances the angular anomaly

\[ S(q, \omega) (1/ \text{keV}) \]

\[ q_1 = \frac{1}{8} \sim (0.37 \text{ Å}) \]

\[ q_3 \]

\[ \text{energy loss (eV)} \]

\[ 2 \quad 4 \quad 6 \quad 8 \quad 10 \]

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \]

\[ 3 \quad \frac{8}{3} \quad \frac{7}{3} \quad 2 \quad \frac{5}{3} \quad \frac{4}{3} \quad 1 \quad \frac{2}{3} \quad \frac{1}{3} \quad 0 \]

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Collective Excitations in Carbon Systems
Experimental verification
by inelastic x-ray scattering
IXS experiments

N. Hiraoka (Spring8, Taiwan)

- elastic tail removed
- uniform scaling
IXS experiments

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

graphite

- angular anomaly close to Bragg reflections
- originates from local field effects (coupling to 1. BZ):
  1. spectrum from $q \rightarrow 0$ reappears (direction of $q_r$)
  2. coupling $\epsilon_{g0}(q_r)$ enforces anisotropy

other systems

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

inhomogenity

3. discontinuity in $S(q, \omega)$ 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

Anomalous Angular Dependence of the Dynamic Structure Factor near Bragg Reflections: Graphite
[accepted by Phys. Rev. Lett. (2008)]

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