Classical theory of light scattering

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Inelastic Light Scattering

I – Linear response theory
   Susceptibility / Fluctuation spectra / Autocorrelation function

II – Macroscopic theory of light scattering
   Vibrational spectroscopies / Origin of the scattering

III – Raman selection rules
   Crystals / Molecules / Polar and non-polar modes (tutorial)

IV – Coherent and incoherent scattering
   Momentum conservation / multiple-order scattering / Effect of disorder
Inelastic scattering experiment

Kinematic conditions

\[
\begin{align*}
\omega_s &= \omega_i \pm \omega \\
\mathbf{k}_s &= \mathbf{k}_i \pm \mathbf{q}
\end{align*}
\]

\((\omega, q)\) frequency and scatt. wavevector probed by the instrument

→ The scattered field \(E_s(t)\) carries the response of the media to an external perturbation, here the incident electric field \(E_i\).
Linear response theory

1. A scattering experiment measures the **response function** of a physical quantity submitted to an external perturbation

   - Physical quantity: polarization, magnetization, displacement, ...
   - External perturbation: electric field, X-Rays, Neutrons, ...

2. The response function is identical to the **spontaneous fluctuation spectra** of that physical quantity
Spontaneous fluctuation spectra

1. Oscillator: e.g. spring-like

\[ G(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_0^T x(t)x(t+\tau)dt \]

Correlation function

\[ G(\tau) = \langle x(t)x(t+\tau) \rangle \]

2. Temporal fluctuations of the scattered intensity \( I(t) \)

\[ \langle I^2 \rangle = \langle I \rangle^2 + \left\{ \langle I^2 \rangle - \langle I \rangle^2 \right\} \exp \left( \frac{\tau}{\tau_0} \right) \]

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Macroscopic Theory of Light Scattering
Spontaneous fluctuation spectra

Oscillator

Relaxator

Fluctuation spectra

\[ S(\omega) \propto \frac{\omega_0^2 \Gamma \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \]

(Damped harmonic oscillator)

\[ S_{osc}(\omega) \propto \frac{\omega_0^2 \Gamma \omega}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \]

(Quasi-elastic)

Quantity measured by a scattering experiment

\[ I_{\text{scatt}}(\omega) \propto S(\omega) \]
The fluctuation spectra $S(\omega)$ of a variable $x(t)$ is the Fourier transform of the autocorrelation function of $x(t)$

$$S(\omega) = TF\left[\langle x(t)x(t+\tau) \rangle\right] = \frac{1}{2\pi} \int_{-\infty}^{+\infty} G(\tau)e^{i\omega\tau} d\tau$$

Quantity measured by a spectrometer !!!

$$I(\omega) = A \times S(\omega)$$

Selection rules:
How $x$ couples to the experimental technique

Response function:
Lineshape of the spectral response
Bridge monitoring

Displacement (in Volts) temporal fluctuations (seconds)

Correlator

\[ G(\tau) = \langle U(t)U(t+\tau) \rangle \]

FT

Power spectrum (in Volts\(^2\))

Almost flat, resonance at \(~2\) Hertz

The power spectra should be as flat as possible, at least around the typical frequencies of moving cars, wind, water,... !!! Otherwise

Also important in buildings (earthquake prevention) and many other engineering applications
# Origin of the scattering

<table>
<thead>
<tr>
<th>Radiation (perturbation)</th>
<th>Scattered intensity</th>
<th>Variable that couples with the incident radiation</th>
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<tr>
<td>X-Rays</td>
<td>$I(\omega, q) \propto FT\left[\langle \rho(0,0)\rho(r,t)\rangle\right]$</td>
<td>Electronic density ($Z$)</td>
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<td>Light</td>
<td>$I(\omega, q) \propto FT\left[\langle E_s(0,0)E_s(r,t)\rangle\right]$</td>
<td>Scattered field (≡ Electrical polarization $P$)</td>
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<td>Elastic deformations (density and shear)</td>
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<tr>
<td>Neutrons</td>
<td>$I(\omega, q) \propto FT\left[\langle b(0,0)b(r,t)\rangle\right]$</td>
<td>Neutron scattering lengths</td>
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</table>
Vibrational spectroscopies

![Graph showing different spectroscopic techniques across the frequency and wavelength spectrum.]

- Raman, IR
- Optic
- X-ray Scattering (XRD)
- Brillouin scattering
- POT
- NSE
- NBS
- TOF-NSE
- XPCS

The graph illustrates the relationship between the scattering wavevector q (Å⁻¹), Wavelength (Å), Frequency (THz), and Energy (meV) for various spectroscopic techniques.
## Origin of the scattering

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Origin of the Scattering
Vibrational spectroscopies

→ Probe the excitations (≡ atomic motions) in solids, liquids and gases

Two types of excitations:

✓ Relaxations → Characterized by a relaxation time

Atomic Diffusion

Molec. flip

Relaxations

Characterized

by a relaxation
time
Vibrational spectroscopies

→ Probe the excitations (≡ atomic motions) in solids, liquids and gases

Optic modes in glasses (light scat.) → incoherent scattering → no q-dependence

Local (molecular) vibrations
Incoherent: No q-dependence

e.g. Normal modes in a triangular planar molecule

Atomic motions are linear combination of all the normal modes

X(t) = X_0 e^{i(\omega_0 t)}
Origin of the scattering

→ Interaction with the electronic shell

- **For an atomic dipole vibrating at** $\omega$:

  Incident field: $E_i = E_0 e^{i(k_i r - \omega t)}$

  Induced dipole: $p = \bar{\alpha} E_i$

  Polarizability

  Expansion of $\bar{\alpha}$ close to its equilibrium position:

  $\alpha = \alpha_0 + x(t) \left( \frac{\partial \alpha}{\partial x} \right)_0$

  At equilibrium
displacement

  Scattered field (radiating dipole):

  $E_s(R, t) = -\frac{\omega_i^2 p(t)}{4\pi \varepsilon_0 c^2 R} \hat{n_s}$

Scattered field $E_s$

(video: wikipedia)
For an atomic dipole vibrating at $\omega$:

\[ E_s \propto p = \alpha E_i, \quad E_i = E_0 \cos(\omega_i t) \quad \Rightarrow \quad p = (\alpha_0 + x(t) \alpha') E_i \quad \text{with } x(t) = x_m \cos(\omega t) \]

\[ p = \alpha_0 E_0 \cos(\omega_i t) + \frac{E_0}{2} x_m \left( \frac{\partial \alpha}{\partial X} \right) \cos[(\omega_i - \omega)t] + \frac{E_0}{2} x_m \left( \frac{\partial \alpha}{\partial X} \right) \cos[(\omega_i + \omega)t] \]

\[ \omega_i \quad \omega_d \quad \alpha' = \frac{\partial \alpha}{\partial X} \neq 0 \quad \Rightarrow \quad \text{fluctuations of the polarizability} \]

Elastic scattering

Stokes

Spectral response at $\pm \omega$

Anti-Stokes

Inelastic scatt. requires $\alpha' \neq 0$
Scattered field \( E_s(R, t) = -\frac{\omega_i^2 \mathbf{p}(t)}{4\pi \varepsilon_0 c^2 R} \hat{n}_s \)

- Fluctuation of the polarization: \( \overline{\alpha'} x(t) E_0 \cos \omega_i t \ \hat{n}_i \)

\[
{E_s(R, t) = -\frac{\omega_i^2 E_0 \cos \omega_i t}{4\pi \varepsilon_0 c^2 R} (\hat{n}_s \overline{\alpha'} \hat{n}_i) x(t)}
\]

- The detector measures the time average of the squared scattered field

\[
\langle E_s, E_s^* \rangle = \left( \frac{\omega_s^4 E_0^2}{16\pi^2 c^4 R^2} \right) (\hat{n}_s \overline{\alpha'} \hat{n}_i)^2 \langle x(t) \rangle \langle x(t + \tau) \rangle
\]

- The spectrometer takes the Fourier transform

\[
TF\{\langle E_s, E_s^* \rangle \} = \left( \frac{\omega_s^4 E_0^2}{16\pi^2 c^4 R^2} \right) (\hat{n}_s \overline{\alpha'} \hat{n}_i)^2 \left\{ \frac{TF\{\langle x(t) \rangle x(t + \tau) \}}{} \right\}
\]

Response function \( S(\omega) \)
Scattered Intensity

\[ I(\omega) \propto \]

\[ \text{Spectrometer} \]

\[ \rightarrow \text{TF}[E_s(t)] \propto \]

\[ \text{Scattered photons with } \neq \text{ phase } \& \neq \text{ optical path in the spectrometer} \]
Scattered field \( E_s(R, t) = -\frac{\omega_i^2 p(t)}{4\pi \varepsilon_0 c^2 R} \hat{n}_s \)

- Fluctuation of the polarization: \( \overline{\alpha'} x(t) E_0 \cos \omega_i t \hat{n}_i \)

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TF\{\langle E_s, E_s^* \rangle\} = \left(\frac{\omega_s^4 E_0^2}{16\pi^2 c^4 R^2}\right) \left(\hat{n}_s \overline{\alpha'} \hat{n}_i\right)^2 TF\{(x(t))x(t + \tau)\}\]

Response function \( S(\omega) \)
• For a collection of molecules

\[ V(E_i, k_i) \]

\[ (E_s, k_s) \]

Induced dipole \( P^{(1)} \)

**Scattered electric field**

- Integral over the N molecules in the scattering volume V

\[ E_s^V = NE_s^{Mol.} \]
Linear response theory:

The scattered intensity is the Fourier transform of the correlation function of the scattered field

$$I_S(\omega, R) = TF\{\langle E^*_S(R, 0)E_S(R, t) \rangle\}$$

$$I_S(R, \omega) = N \left( \frac{\omega_S^4 E_0^2}{16\pi^2 c^4 R^2} \right) \left| n^i \alpha^{ij} n^j \right|^2 S(\omega)$$

1/\lambda^4 as for Rayleigh scattering

Raman selection rules (Intensity factor)

Response function (lineshape)

[Wiener Khintchine theorem]
Phonon population

\( \omega_i, k_i \)

\[ \hbar \omega = \hbar \omega_i - \hbar \omega \rightarrow n(\omega) + 1 \]

Stokes

Creation of a phonon

\[ \hbar \omega = \hbar \omega_i + \hbar \omega \rightarrow n(\omega) \]

Anti-Stokes

Anihilation of a phonon

\( \omega_s, k_s \)

Energy loss for the incident radiation

\( \hbar \omega_s = \hbar \omega_i - \hbar \omega \rightarrow n(\omega) + 1 \)

Energy gain for the incident radiation

\( \hbar \omega_s = \hbar \omega_i + \hbar \omega \rightarrow n(\omega) \)
Response function

- Damped harmonic oscillator (DHO)

\[ S_i(\omega) \propto [n(\omega) + 1] \frac{\Gamma_{0i}\omega}{(\omega_{0i}^2 - \omega^2)^2 + \Gamma_{0i}^2\omega^2} \]  
(stokes)

- Or Lorentzian (limit \( \omega_0 \gg \Gamma_0 \))

\[ S_i(\omega) \propto [n(\omega) + 1] \frac{\Gamma_{0i}}{(\omega_{0i} - \omega)^2 + (\frac{\Gamma_{0i}}{2})^2} \]  
(stokes)

Bose-Einstein population factor

\[ n(\omega) = \frac{1}{e^{\frac{\hbar\omega}{k_BT}} - 1} \]

Anti-stokes \([n(\omega) + 1] \rightarrow n(\omega)\)

- In glasses:

\[ S_i(\omega) = \text{gaussians} \quad \text{(see after...)} \]
Bose Factor

\[ n(\omega) = \frac{1}{e^{\omega/k_B T} - 1} \]

Much less intensity on anti-stoke side!
Inelastic scattering experiment

A scattering experiment measures the fluctuation spectrum of the scattered field

Kinematic conditions

\[ \omega_s = \omega_i \pm \omega \]
\[ k_s = k_i \pm q \]

\((\omega, q)\) frequency and scatt. wavevector probed by the instrument

**Fluctuation spectra** \( S(\omega) !!! \)
Raman selection rules
Vibrations are active in Raman only if

$$\alpha' = \left( \frac{\partial \alpha}{\partial X} \right)_0 \neq 0$$

**Exemple for CO\textsubscript{2} :**

- **Raman active**
  - \( \left( \frac{\partial \alpha}{\partial X} \right)_0 \neq 0 \)

- **Raman inactive**
  - \( \left( \frac{\partial \alpha}{\partial X} \right)_0 = 0 \)
Polarization analysis

\[ P = \alpha . E_i \]

\[ \begin{align*}
    P_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\
    P_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\
    P_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z
\end{align*} \]

Induced dipole

If \( E_i \) is polarized \( \parallel e_x \):

- \( P_x, P_y, P_z \neq 0 \) (if \( \alpha_{xx}, \alpha_{yx}, \alpha_{zx} \neq 0 \))

- The direction of the induced dipole \( \neq \) direction of \( E_i \) …

… and it is the same for the scattered field \( E_s \)

\[ \rightarrow \text{Polarisation analysis provides information on the molecular symmetry} \]
**Crystalline selection rules**

Ordered atoms give coherent scattering but $q \approx 0 \rightarrow I_s$ independent of $q$

$$I_s(q, \omega, R) \propto \left( \frac{\omega_s^4 E_0^2}{16 \pi^2 c^4 R^2} \right) \left| n_s^i \alpha'^{ij} n_s^j \right|^2 S(q, \omega)$$

Raman selection rules

(Intensity factor)

For Crystals

$$n_S \begin{bmatrix} \alpha'_{11} & \alpha'_{12} & \alpha'_{13} \\ \alpha'_{21} & \alpha'_{22} & \alpha'_{23} \\ \alpha'_{31} & \alpha'_{32} & \alpha'_{33} \end{bmatrix} n_I$$

$I_s$ depends on the polarization of the incident and scattered fields
Polarizability tensors are tabulated in Raman books for all active modes and all molecular symmetries.
Raman in crystals: $\beta$-quartz

A1: non-polar mode:

$$\alpha = \begin{bmatrix} a & . & . \\ . & a & . \\ . & . & b \end{bmatrix}$$

$$I^{RS} \propto |n_{S} \begin{bmatrix} a & . & . \\ . & a & . \\ . & . & b \end{bmatrix} n_{I}|^2$$

$$I^{RS} \propto a^2$$

$$I^{RS} = 0$$

How does it works in liquids and gases (no crystallographic directions)?
Raman in liquids and gases

- Symmetry elements → point group, e.g. CCl$_4$ tetrahedra ($T_d$)

- Average over all orientations of the molecules

$$I_{RS} \propto \left\langle \left| n_I m_J \alpha_{IJ} \right|^2 \right\rangle$$

- $\alpha_{IJ}$ in the laboratory frame in terms of $\alpha_{pq}$ in the molecular frame:

$$\alpha_{IJ} = \sum_{p=1}^{3} \sum_{q=1}^{3} E_{Ip} E_{Jq} \alpha_{pq}, \quad E : \text{Rotation matrix defined by the Euler angles}$$
Raman in liquids and gases

- Incoherent scattering \( \propto \) average of the intensity arising from one molecule with all possible orientations

\[
I_{I \leftrightarrow f}^{RS} \propto \langle R_{I \leftrightarrow f} \rangle = \int_0^{2\pi} d\alpha \int_{-\pi}^{\pi} d\gamma \int_0^\pi \sin \beta d\beta
\]

\[
\times \sum_p \sum_{q'} \alpha_p^q \alpha_{q'}^p E_p E_{q'} E'_{p'} E'_{q'}
\]


**Anisotropic disorder**: integral over angular limits defining the molecular orientations

**Isotropic disorder**: Integral over the full angular range

The integration gives rise to a simple expression
Two measurable quantities:

\[ I_{\parallel} = \frac{1}{5} \sum_i \alpha_{ii}^2 + \frac{2}{15} \sum_{i<j} \alpha_{ii} \alpha_{jj} + \frac{4}{15} \sum_{i<j} \alpha_{ij}^2 \]

\[ I_{\perp} = \frac{1}{15} \sum_i \alpha_{ii}^2 - \frac{1}{15} \sum_{i<j} \alpha_{ii} \alpha_{jj} + \frac{4}{15} \sum_{i<j} \alpha_{ij}^2 \]

**Example**: planar triangular molecules in D_{3h} point group

Depolarization ratio:

\[ \rho = \frac{I_{\perp}}{I_{\parallel}} \leq \frac{3}{4} \]

Species \( E' \):

\[
\begin{pmatrix}
d & \cdot & \cdot \\
\cdot & -d & \cdot \\
\cdot & \cdot & \cdot \\
-d & \cdot & \cdot \\
\cdot & \cdot & \cdot 
\end{pmatrix}
\]

\[ \rho = \frac{3}{4} \]

Species \( A_{1}' \):

\[
\begin{pmatrix}
a & \cdot & \cdot \\
\cdot & a & \cdot \\
\cdot & \cdot & b 
\end{pmatrix}
\]

\[ \frac{1}{\rho} = \frac{I_{\parallel}}{I_{\perp}} = \frac{5}{3} \left(\frac{2a + b}{a - b}\right)^2 + \frac{4}{3} \]
Raman in glasses

Single molecule

\( I_0(\omega) \)

- Homogeneous broadening

\( N \) Non–interacting identical molecules

\( \sim N \cdot I_0(\omega) \)

- Incoherent Scattering

\( N \) Non–interacting non-identical molecules

\( I(\omega) \)

- In-homogeneous broadening

\( N \) interacting non-identical molecules

- Modulation of \( I(\omega) \) due to molecular coupling

(suppose no shift in \( \omega \))

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Macroscopic Theory of Light Scattering
Summary

**Theoretical framework**

- Crystals
- Liquids and gases
- Glass

- Response function
- Selection rules

\[ I_{RS}^{\sigma}(\omega) \propto R_{\sigma}(\omega) \frac{[n(\omega) + 1]}{\omega} S_{\sigma}(\omega) \]

- **Crystals**: Damped harmonic oscillator
- **Liquids and gases**: Selection rules
- **Glass**: \( g_{\sigma}(\omega) \) - density of states of mode \( \sigma \)

- \( C_{\sigma}(\omega) \) - unknown

- No theory \( \rightarrow \) numerical simulations

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Macroscopic Theory of Light Scattering
- IV -

Coherent vs incoherent scattering
1/ Extended modes  

Optic modes in Crystals  
Acoustic modes  

\[ X(r, t) = X_0 e^{\pm i(Qr - \Omega t)} \]

**Q**: Wave-vector of the excitation  
**\Omega**: Frequency of the excitation  

**Plane wave**  

**Macroscopic Theory of Light Scattering**

\[ E_i = E_0 e^{i(k_ir - \omega t)} \]

\[ \delta p = \varepsilon_0 \chi' X(r, t) E_i \]

\[ E_s = \int_V \delta p e^{-ik_s r} dV \]

\[ E_s \propto E_0 \int_V \chi' X_0 e^{i[(k_i - k_s \pm Q)r - (\omega_i \mp \Omega)t]} dV \]

\[ E_s \neq 0 \text{ only if } k_i - k_s \pm Q = 0 \]

**Q = q = \pm (k_i - k_s)**

The experiment sees the excitations whose wave-vector \( Q \) matches that of the experiment (scattering wave-vector \( q \))
$Q = q = \pm (k_i - k_s)$

→ Momentum conservation

Coherent scattering

Sample

(010) $k_s$

$Q \parallel (110)$

(100) $k_i$

$q$ $Q \parallel (110)$

Sample

(110) $k_s$

$q$ $Q \parallel (010)$

$\omega, \Omega$

$\sim 10^{-3} \text{ Å}^{-1}$

$\pi/a \sim 1 \text{ Å}^{-1}$

$ZB$

$\pm q_x, Q_x$

$\pm q_y, Q_y$

Flat dispersion surfaces at $Q \rightarrow 0$

$I_{LS}^{\text{optic}}$ independent on the direction of $Q$

Elastic constants change with $Q$

$I_{LS}^{\text{acoustic}}$ depends on the direction of $Q$

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Macroscopic Theory of Light Scattering

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2/ Local vibrations

Molecular (optic) vibrations

\[ X(r, t) = X_0 e^{\pm i \Omega t} \]

\[ E_S \propto E_0 \chi' X_0 e^{-i(\omega_i \mp \Omega t)} \]

\[ \rightarrow \quad Q \text{ is not a relevant quantum number} \]

\[ \text{No constraint on } q \]

The vibration scatters at every \( q \) values

Gases and Liquids

\[ \omega \]

Optic branches (flat)

At the wavelengths of light, optic modes in glass behave as incoherent scatterers

Acoustic branches

\[ \text{Collectives modes (\( \equiv \) crystals) } \]
3/ quasi-local vibrations

Glasses

Structural disorder

Spatial coherence length $L$ is short

$$X(r, t) = X_0 e^{-r/L} e^{\pm i(\Delta Q \cdot r - \Omega t)}$$

$L \ll \lambda_i, \lambda_s$

Spatial Localization

$\Delta Q \propto \frac{1}{L}$

TF

Wave-vector spectral broadening

$$\Delta Q = q = \pm (k_i - k_s)$$

The contribution at $\omega = \Omega$ is the sum over all modes having a wave-vector spectral component $\Delta Q$ which matches the scattering wave-vector $q$

At the wavelengths of light, optic modes in glass behave as incoherent scatterers ($\sim$ liquids)
1D-diatomic linear chain with spring disorder

(Toy model for glass)

[B. Rufflé, B. Hehlen, Arxiv:1908.08321]
1D-diatomic linear chain with spring disorder

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1D-diatomic linear chain with spring disorder
(Toy model for glass)

Vibrations in glasses: smeared out version of the corresponding crystal

[B. Rufflé, B. Hehlen, Arxiv:1908.08321]
Molecular selection rules are usually lifted by structural distortions and couplings.

A « molecular » analysis is an over-simplified approach, but ...

Selection rules partially (or fully !!) apply when:
- the glass has well defined structural units
- the modes are decoupled from the network

Broadening of the spectral lines:
- Distribution of bond lengths, bond angles → Inhomogeneous spectral broadening
- Spatial localisation → wave-vector spectral broadening
Raman spectra of vitreous silica

VV-Spectra

Motions of rigid SiO$_4$ tetrahedra coupled to translations

[B Galeener et al., 70's-80's]
[Pasquarello et al., PRL (2003)]

Si-O-Si stretching

[Taraskin, Elliott PRB 1997]

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Macroscopic Theory of Light Scattering
Raman spectra of vitreous boron oxide $\text{B}_2\text{O}_3$
Raman spectra of vitreous boron oxide $\text{B}_2\text{O}_3$

Boson peak librations ($E''$) & translations of rigid units

$A_2''$ (polar)
Out-of-plane motions

$A_1'$

$E'$ (polar)
In-plane motions

[G. Simon et al. PRB 2007]
Aknowledgements:
   Pr. E. Courtens & R. Vacher (private communications)

Bibliography:
   Hayes & Loudon
   Poulet & Mathieu
Light scattering by vibrations

- II -

Raman scattering in simple glasses

Laboratoire Charles Coulomb
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I- General information obtained from *ab-initio MD* simulations

*Silica / Sodo-silicates*

II- Bending vibrations and Si-O-Si bond angle distribution

*Densified silica / Sodo-silicates*

III- Cations modes and cation sites

*Aluminosilicates*

IV - $Q_n$-modes and $Q_n$ species

*Sodo-silicates*
MD-simulations of Raman spectra of sodosilicates

✓ 3 compositions

\[
\begin{align*}
\text{Na}_2\text{O}-4\text{SiO}_2 \, (\text{NS4}) \\
\text{Na}_2\text{O}-3\text{SiO}_2 \, (\text{NS3}) \\
\text{Na}_2\text{O}-2\text{SiO}_2 \, (\text{NS2})
\end{align*}
\]

2 samples/composition

~200 atoms/sample

[D. Kylimis et al. PRB2019]
Atomic contribution of the Raman active modes

- Oxygen contribution dominates the spectra
- Sodium contribute at low frequency
Mode decomposition of the Vibrational density of states

![Graph showing vibrational density of states with modes labeled as Rocking, Bending, and Stretching.](image)
- The Narrowing of the band at ~500 cm\(^{-1}\) not well reproduced

- The multimodal Q\(_n\) spectral response qualitatively reproduced by MD, but deviations in the relative intensities
Raman spectroscopy of v-SiO$_2$ at room pressure

- VV-Spectra

- Motions of rigid SiO$_4$ tetrahedra coupled to translations

- Si-O-Si stretching

- [Galeener et al., 70's-80's]
- [Pasquarello et al., PRL (2003)]

- R-Band
- Ring modes

- TO$_{1,2}$
- TO$_3$
- D$_2$
- D$_1$
- Polar modes

- [Taraskin, Elliott PRB 1997]
- [Hehlen, et al. PRL 2000]
## Atomic vibrations: visual inspection

<table>
<thead>
<tr>
<th>Collective motions of SiO$_4$ tetrahedra</th>
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<tr>
<td>Na-NBO Stretch</td>
<td>Na-NBO_stretch_ns4-351cm-1.mp4</td>
</tr>
<tr>
<td>4-fold ring breathing</td>
<td>4member_477cm-1.mp4</td>
</tr>
<tr>
<td>Si-O-Si bending &amp; 3-fold ring breathing</td>
<td>3member_610cm-1.mp4</td>
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<td>BO &amp; NBO stretching</td>
<td>asymm-NBOstretch_957cm-1.mp4</td>
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[D. Kylimis et al. PRB 2019](#)
I- General information obtained from *ab-initio MD* simulations

*Silica / Sodo-silicates*

II- Bending vibrations and Si-O-Si bond angle distribution

*Densified silica / Sodo-silicates*

III- Cations modes and cation sites

*Aluminosilicates*

IV - $Q_n$-modes and $Q_n$ species

*Sodo-silicates*
Permanently densified silicas, $d$-SiO$_2$

- **Permanent densification**

$$\rho = 2.21 \rightarrow 2.63 \text{ g/cm}^3$$

- Reduction of the Si-O-Si angle $\theta$ in the network

- SiO$_4$ tetrahedra remain unchanged  
  [Y.Inamura *et al.* JNCS 2001]

  $\rightarrow$ Puckering of the ring network + bond redistribution

  $\rightarrow$ Ring statistic $\downarrow$ towards smaller ring sizes

- **3 glasses have been investigated**:

  $$\rho = 2.21, 2.41, \text{ and } 2.63 \text{ g/cm}^3$$

  10% densification \quad 20% densification
Permanently densified silicas, $d$-SiO$_2$

- **Raman scattering of bending modes**

Frequency up-shift of the R, D1 and D2 bands

→ Reduction of the Si-O-Si angle
• Central force model of coupled tetrahedra

\[ \alpha : \text{O-Si restoring force constant} \]

\[ \theta : \text{inter-tetrahedra effective coupling constant} \]

\[ \omega_R^2 = \frac{\alpha}{m} (1 + \cos \theta) \quad \text{O-Bending (R-band, } \omega_R) \]

• Relation with Raman signal

\[ I_{\sigma}^{RS}(\omega) \propto C_{\sigma}(\omega) \rho \frac{(n(\omega) + 1)}{\omega} g_\sigma(\omega), \quad \text{with} \]

\[ C_B(\omega) \propto \omega^2 \]

\[ g_B(\omega) \propto \frac{1}{\rho} \frac{I_{B}^{RS}(\omega)}{\omega \cdot [n(\omega) + 1]} \]

Assuming \( \alpha \) constant \( \Rightarrow \omega \propto \cos \theta / 2 \)

\[ \text{Frequency to angle conversion} \]
~ Angular distribution of Si-O-Si angles
Si-O-Si angle $\theta$ in $d$-SiO$_2$

Network angle:

- $n \approx 6$  Max. of the distribution
- $n > 6$  Average angle

Small rings:

- $n = 3$
- $n = 4$

[B. Hehlen, J.Phys.: Cond Matter 2010]

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Macroscopic Theory of Light Scattering
Si-O-Si angle $\theta$ in $d$-SiO$_2$

**Network angle:**
- $n \approx 6$ Max. of the distribution
- $n > 6$ Average angle

**Small rings:**
- $n = 3$
- $n = 4$

---

[B. Hehlen, J. Phys.: Cond Matter 2010]

[Devine et al. 1987]

[Rahmani et al. PRB, 2003]

[Matsubara, Ispas, Kob, 2009]
Density of small rings in $d$-SiO$_2$

*Comparison Raman / ISRS*

- $2.20 \text{ g/cm}^3$
  - $D_1$: 1 Ring / 555 SiO$_2$
  - $D_2$: 1 Ring / 670 SiO$_2$

- $2.63 \text{ g/cm}^3$
  - $D_1$: 1 Ring / 380 SiO$_2$
  - $D_2$: 1 Ring / 150 SiO$_2$

*Pasqurello et al. PRL 2003*

*J. Burgin et al. PRB 2008*

Concentration of small rings is very small

Increase of the threefold rings (denser structures)

Concentration of fourfold rings $\approx \text{Cte}$

Possible scenario upon densification:

large rings ($n \geq 5$) $\rightarrow$ 4-fold rings ($D_1$)

4-fold rings ($D_1$) $\rightarrow$ 3-fold rings ($D_2$)
Sodo-silicate glasses

Cation modifiers:
- Depolarize the network
- Create Non-Bridging oxygens
Si-O-Si angle

Density of states of bending modes

Bimodal angular population in sodo-silicates:
- A narrow and peaked one at high frequency
- A broad one at lower frequency

SiO$_2$
- 40%Na$_2$O $\rightarrow$ NS1.5
- 33%Na$_2$O $\rightarrow$ NS2
- 25%Na$_2$O $\rightarrow$ NS3
- 20%Na$_2$O $\rightarrow$ NS4
Distribution of Si-O-Si angles

\[ \text{SiO}_2, \ 4\text{SiO}_2: \text{Na}_2\text{O (NS4)}, \ 2\text{SiO}_2: \text{Na}_2\text{O (NS2)} \]

From Raman scattering

From Computer simulations
Si-O-Si angle

Most probable angle (max. of the distribution)

Δθ ≈ -0.3°/mol%Na

[B. Hehlen et al. JNCS2017]
Bimodal distribution of Si-O-Si angles

- In sodo silicates

**From Raman scattering**

*Bimodal angular distribution: angles are weaker in Si-O-Si bonds close to Cations*

[B. Hehlen et al. JNCS2017]

**From Computer simulations**

- $Q_4$-O-$Q_4 \rightarrow 144.2^\circ$
- $Q_4$-O-$Q_3 \rightarrow 143.8^\circ$
- $Q_4$-O-$Q_2 \rightarrow 141.2^\circ$
- $Q_3$-O-$Q_3 \rightarrow 140.1^\circ$
- $Q_3$-O-$Q_2 \rightarrow 137.3^\circ$

[D. Kylimis et al. PRB 2019]
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Sodosilicates and Aluminosilicates

IV - $Q_n$-modes and $Q_n$ species

Sodo-silicates
✓ Depolarized Raman spectra (VH) sensitive to cation motion

→ *Information on their local environment*

*e.g.* Network modifier or charge compensator

[Hehlen & Neuville JPCB2015]
Sodosilicates (VH spectra)

→ All cations are network modifiers

ω₁ ≈ 150 cm⁻¹

ω₂ ≈ 330 cm⁻¹

BP+ tail:
Modified log-normal function
Cutoff around 500 cm⁻¹

Two cation modes:

ω₁: gaussian function
(though probably asymmetric shape)

ω₂: gaussian function
### Atomic vibrations: visual inspection

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#### Vibrational Modes
- 4-fold ring breathing
- Si-O-Si bending & 3-fold ring breathing
- BO & NBO stretching

**Raman response of cation modes**

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Macroscopic Theory of Light Scattering
Cations modes in aluminosilicates

✓ **Alkaline earth**

\[ \text{RO} \rightarrow \text{CaO, SrO, BaO} \]

✓ **Alkali**

\[ \text{R}_2\text{O} \rightarrow \text{Na}_2\text{O} \]

\[ R = \frac{[\text{RO}]}{[\text{Al}_2\text{O}_3]} \]
High-frequency mode $\omega_2$

NAS
(Na$_2$O)

$\omega_1$  $\omega_2$

![Graph showing NAS (Na$_2$O) with frequencies $\omega_1$ and $\omega_2$. The graph includes a plot of $\sqrt{H(\omega)}$ vs. frequency (cm$^{-1}$) for different Na$_2$O concentrations.](image)

[Hehlen & Neuville JPCB2015]
High-frequency mode $\omega_2$

Alkali

NAS
$(Na_2O)$

CAS
$(CaO)$

Alkali earth

$\omega_1$  $\omega_2$

$\omega_2$

[Hehlen & Neuville JPCB2015]
High-frequency mode $\omega_2$

Alkali
NAS (Na$_2$O)
CAS (CaO)

Alkali earth
SAS (SrO)

[Hehlen & Neuville JPCB2015]

[Hehlen & Neuville TBP]
Cation modes $\omega_1$ and $\omega_2$

$\omega_1$ decreases as $\omega_2$ decreases the cation content

$\rightarrow I(\omega_1)$ decreases as decreases the cation content

$\rightarrow I(\omega_2)$ decreases much faster than $[\text{Cation}]$

$\rightarrow$ disappears at $R \approx 1$
Low frequency mode, $\omega_1$

Intensity $\rightarrow 0$ when $[\text{Cation}] \rightarrow 0$  \quad \rightarrow \quad \text{All cations participate to } \omega_1
High frequency mode $\omega_2$

$\omega_2$ decreases faster than the cation content

[Hehlen & Neuville submitted to JPCB]
In the alumino silicates, the intensity reaches zero for $[\text{Cation}]_{\text{Modif}} \approx 0$ !!

$\omega_2$ decreases faster than the cation content

Deviation at low values: $[\text{Al}]^{V}, [\text{Al}]^{VI}$ ?

$\omega_2$ in the high frequency mode

[Hehlen & Neuville submitted to JPCB]
Cations modes

$\omega_1$: all cations (dangling)

$\omega_2$: only network modifier cations (stretching)
I- General information obtained from *ab-initio MD* simulations

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*Densified silica / Silica under pressure / Sodo-silicates / Borosilicates*

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*Aluminosilicates*

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Atomic vibrations: $Q_n$ species

- Collective motions of SiO$_4$ tetrahedra
- Na-NBO dangling Si-O-Si bending
- 3-fold ring breathing
- BO & NBO stretching

Raman response of $Q_n$ species

BO & NBO stretching

asymm-NBOstretch_957cm-1.mp4

asymm-NBOstretch_1130cm-1.mp4
Calculated Raman spectra: Response of $Q_n$-species

Contributions per $Q_n$-species

- The contributions are multimodal or asymmetric (not gaussians)!!!
- Their shape does not change much with Na contents
- Strong overlap between the $Q_n$ vibrational responses

Shapes:

- Scattering efficiency of each $Q_n$ species is glass-independent

Intensities (area):

**References:**

- [Kylimis et al. PRB2019]

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Macroscopic Theory of Light Scattering

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Reconstruction of the total $Q_n$ Raman-response

Each spectral shape is weighted by the right amount of $Q_n$ in the glass

Fairly good agreement with experiment!!
✓ Raman scattering provides an indirect way to probe local and medium range structure of glasses

✓ **Vibrational mode analysis** can be very powerful in simple glasses, in particular when coupled with **numerical simulations**

✓ ... But becomes limited in complex glasses owing to mode broadening and overlapping

✓ In that case **statistical spectral analyses** (e.g. PCA) might be better