An introduction to vibrational properties of glass models

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Outline

- *Introduction*
- **1st Part : Vibrational density of states (VDOS) of the glass models**
  1. **Computation of the dynamical matrix : analytical calculation and finite differences method**
  2. **Diagonalization of the dynamical matrix : eigenvectors and eigenvalues sets**
  3. **True VDOS $g(\omega)$ and partial VDOS $g_\alpha(\omega)$**
- **2nd Part : Connection to experimental results : VDOS extracted from neutron diffraction**
- **3rd Part : Mode Analysis : participation ratio, acoustic/optic like mode, rocking,bending, stretching etc.**
- **4th Part : IR Spectra**
- **5th Part : Raman Spectra**

Vibrational spectra

Experimentally, they can be measured/extracted from :

- Neutron scattering
- Infrared measurements
- Raman, hyper-Raman experiments

For a given structural model, these spectra can be, in principle, computed : using first-principles methods, theoretical models or autocorrelation functions.

1st part : Vibrational density of states (VDOS)

- The phonon density of states (VDOS) over frequency $g(\omega)$ represents the nb. of vibrational states having a frequency in the range ω and $\omega + \mathrm{d}\omega$

$$g(\omega) = \frac{1}{3N-3} \sum_{k=4}^{3N} \delta(\omega - \omega_k)$$

- Within the harmonic approximation (i.e. small atomic displacements from their equilibrium positions), $g(\omega)$ can be numerically computed using 2 methods :
  - the Fourier transform of the velocity autocorrelation function

$$g(\omega) \propto \int_0^\infty \frac{1}{k_B T} \sum_j m_j \langle \mathrm{v}_j(t) \cdot \mathrm{v}_j(0) \rangle \exp(-\imath\omega t) dt$$

  - diagonalization of the dynamical matrix

Dynamical matrix

- Given a structural model containing N atoms, characterized by a potential energy $\mathcal{U}(\{\mathrm{r}^N\})$ (classical or ab initio approach)
- Any atomic vibration $\equiv$ a linear combination of the normal modes, i.e. the eigenvectors of the dynamical matrix $\{\mathrm{e}^n,\ n = 1, \ldots, 3N\}$)

(1) $$\sum_{j,\beta} D_{i,\alpha;j,\beta}\, e^n_{j\beta} = \omega_n^2 e^n_{i\alpha}$$

with

(2) $$C_{i,\alpha;j,\beta} = \left(\frac{\partial^2 \mathcal{U}(\{\mathrm{r}^\mathrm{N}\})}{\partial r_{i,\alpha} \partial r_{j,\beta}} \right)_{\{\mathrm{r}^0\}}$$ and $$D_{i,\alpha;j,\beta} = \frac{1}{\sqrt{m_i m_j}} C_{i,\alpha;j,\beta}$$

- The set of 3N-component vectors e^n is linked to the real space displacement $\mathrm{u}^n_{i,\alpha} \approx \frac{1}{\sqrt{m_i}} \mathrm{e}^n_{i,\alpha}$

Dynamical matrix (2)

- Methods for computing the dynamical matrix :
  - analytical calculation in a classical MD approach, for an effective potential with a given functional form $\mathcal{U} = \mathcal{U}(\{\mathrm{r}^{\mathrm{N}}\})$
  - numerical calculation, by finite differences method

$$\begin{aligned} C_{i,\alpha;j,\beta} &= \left(\frac{\partial^2 \mathcal{U}(\{\mathrm{r}^{\mathrm{N}}\})}{\partial r_{i,\alpha} \partial r_{j,\beta}}\right)_{\{\mathrm{r}^0\}} \\ &\approx \frac{f_{j,\beta}(\ldots, r_{i,\alpha} + \Delta, \ldots) - f_{j,\beta}(\ldots, r_{i,\alpha} - \Delta, \ldots)}{2\Delta} \end{aligned}$$

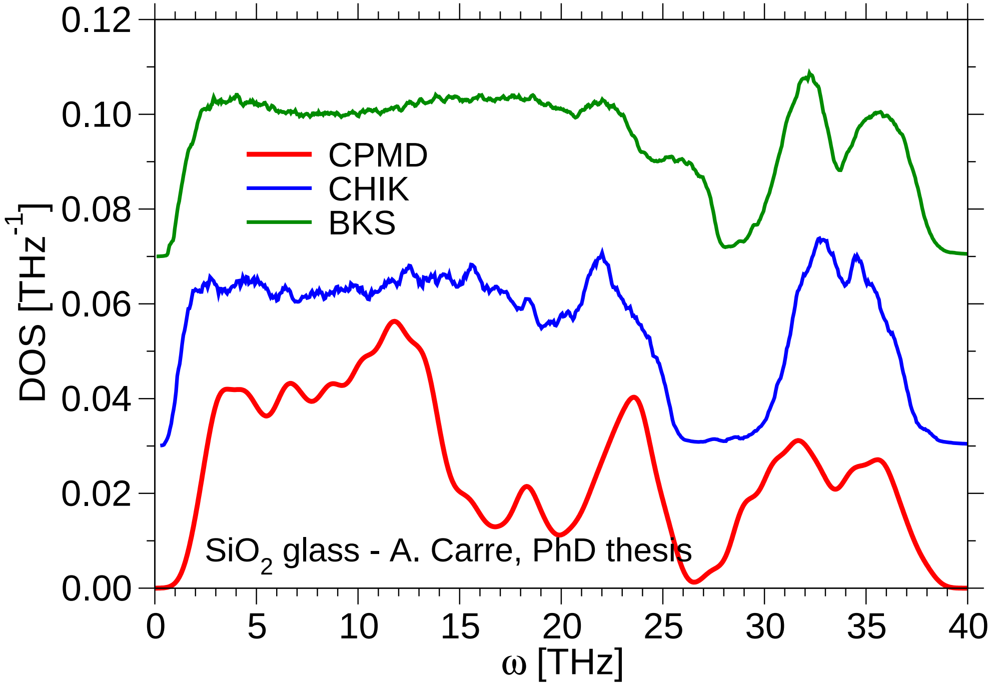
  where $f_{j,\beta}$ is the β component of the forces on atom i.

- Numerical diagonalization $\Rightarrow \{\omega^n, \mathrm{e}^n\}_{n=1,\ldots,3N}$ such that $\sum_i \mathrm{e}_i^n \mathrm{e}_i^m = \delta_{nm}$ and $\sum_n e_{i,\alpha}^n e_{j,\beta}^n = \delta_{ij}\delta_{\alpha\beta}$

True vibrational density of states (VDOS) $g(\omega)$

$$g(\omega) = \frac{1}{3N-3} \sum_{k=4}^{3N} \delta(\omega - \omega_k)$$ - δ functions broadened by Gaussian functions

- In general, the vibrational properties present a strong dependence on the interaction potential



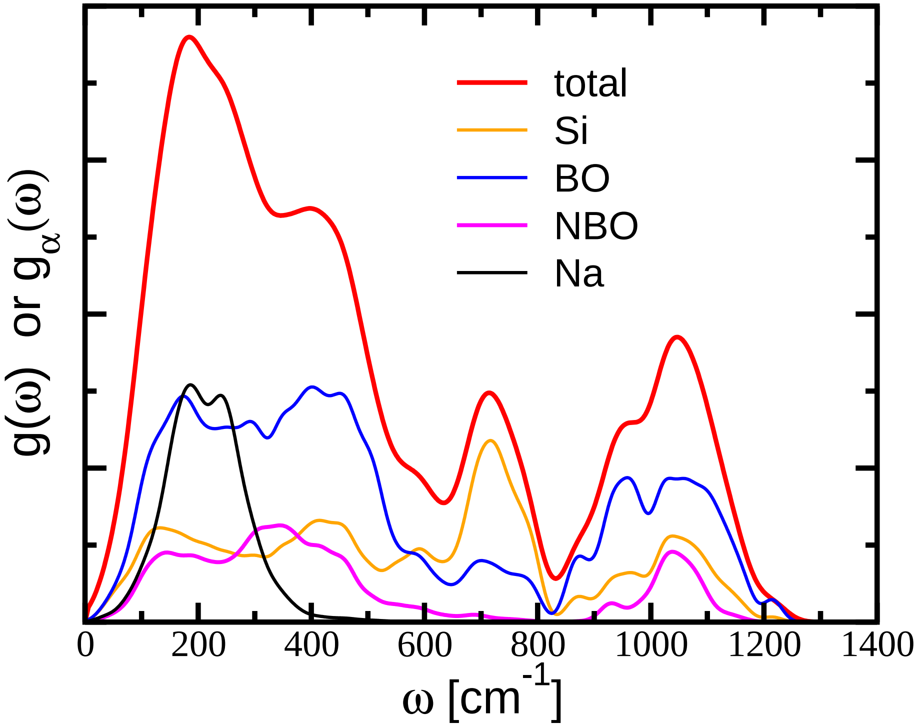
- SiO_2 glass - BKS and CPMD structural models very similar, BUT their VDOS are far from being similar [Benoit and Kob, EPL (2002)].

Decomposition of the VDOS

- Decomposition into partial VDOS $g_\alpha(\omega)$, i.e. according to the weights of the different species :

$$g_\alpha(\omega) = \frac{1}{3N-3} \sum_{k=4}^{3N} \sum_{i\in\alpha} |\mathrm{e}_i^k|^2 \delta(\omega - \omega_k)$$

E.g. For $\alpha =$ Si, BO, NBO, Na in a NS4 glass, Ispas et al. JNCS 2005

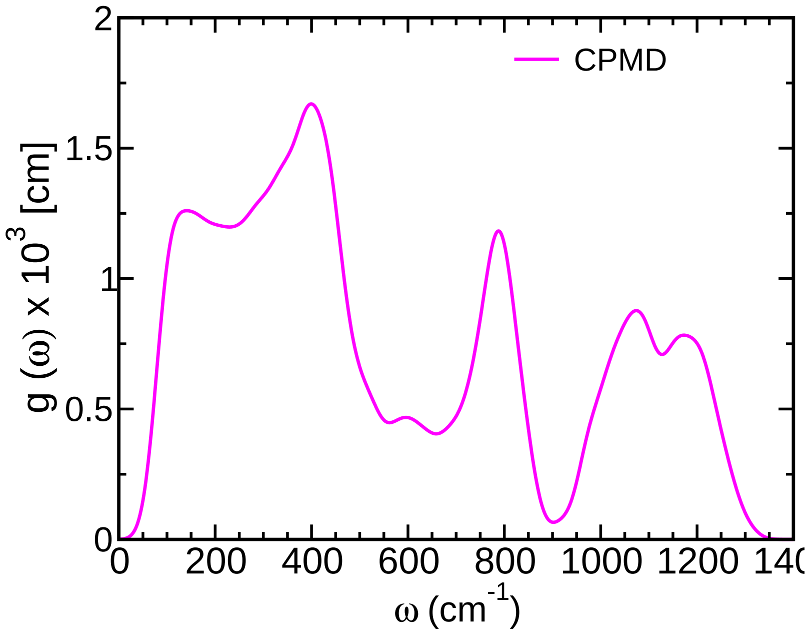


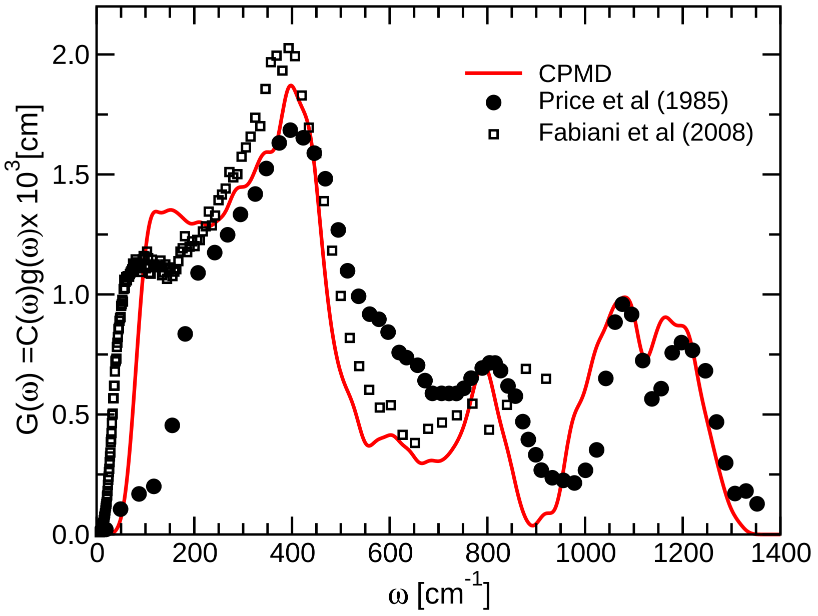
3 main bands (Gaussian broadening FHWM=35 cm^{-1}) :

- **LF bands** ($\leq$ 500 cm^{-1}): Na and O (bending and rocking) motions
- **MF bands** (500-900 cm^{-1}): Si and BO complex motions
- **HF bands** ($\geq$ 900 cm^{-1}): Si-NBO and Si-BO stretching motions

2nd part : VDOS - connection to experimental results

- The dynamical structure factor $S(\mathbf{Q},\omega)$ measured in inelastic neutron scattering (INS) is roughly proportional to the true VDOS ⇒ need to consider approximations and simplifications.
- Taraskin & Elliott [PRB **55** (1997)] - a correction function connecting the true and effective VDOS : $G(\omega) = C(\omega)g(\omega)$, with $G(\omega)$ called effective VDOS





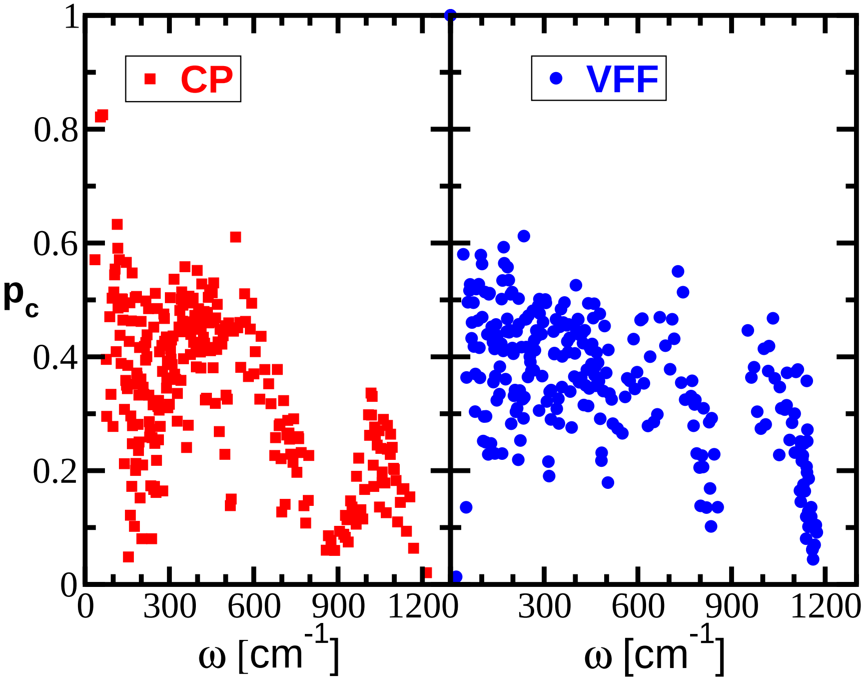
CPMD data - SiO_2 glass [Benoit & Kob EPL (2002)]

3rd part : Analysis of modes

- Complete knowledge of $\{\omega^n, \mathbf{e}^n\}_{n=1,\ldots,3N}$ $\Rightarrow$ detailed analysis of the nature of the vibrational excitations [Taraskin & Elliott, PRB **56** (1997)]
  - participation ratio
  - phase quotient
  - Bridging oxygen motions
  - $\ldots$

Analysis of modes - participation ratio

NS4 glass [Ispas et al. JNCS (2005)] - *ab initio* versus Classical Forces Fields (VFF)



$$p_c(\omega_p) = \frac{\left(\sum_{i=1}^{N} |\mathbf{u}_i(\omega_p)|^2\right)^2}{N \sum_{i=1}^{N} |\mathbf{u}_i(\omega_p)|^4}$$

→ extended mode ≈ 1,

→ strongly localized mode ≈ $1/N$

⇒ *ab initio* (CP) modes are more localized than the classical VFF ones

Analysis of modes - Bridging Oxygen motions

$$S_{\mathrm{BO}}(\omega_p) = \frac{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p) \cdot \hat{\mathbf{r}}_{i-i'}|^2}{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p)|^2}$$

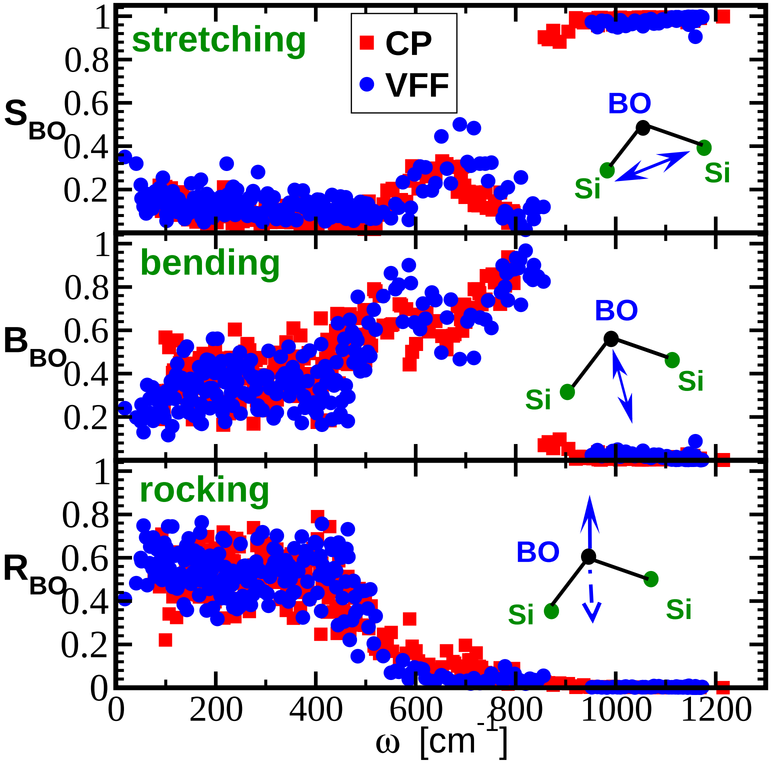
$$B_{\mathrm{BO}}(\omega_p) = \frac{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p) \cdot \hat{\mathbf{r}}_{i+i'}|^2}{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p)|^2}$$

$$R_{\mathrm{BO}}(\omega_p) = \frac{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p) \cdot \hat{\mathbf{r}}_{\Delta}|^2}{\sum\limits_{\mathrm{BO}} |\mathbf{u}_i(\omega_p)|^2}$$

$$S_{\mathrm{BO}} + B_{\mathrm{BO}} + R_{\mathrm{BO}} = 1$$

$$p = 1, 2, \ldots 3 \times N$$

[Bell et al, J Phys C **3** (1970)]



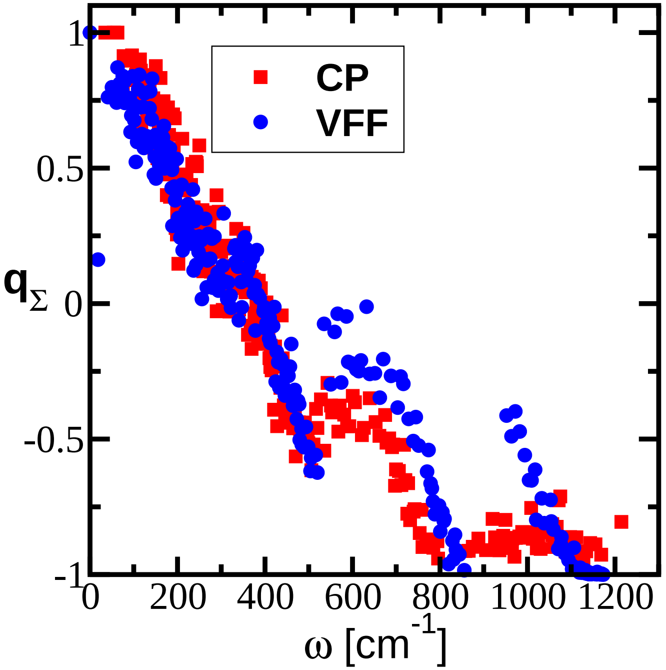
NS4 glass model

- strong frequency dependent
- VFF overestimates the stretching
- in the MF range : stretching/bending mixed motions

Analysis of modes - phase quotient

NS4 glass [Ispas et al. JNCS (2005)]

$$q_{\Sigma}(\omega_n) = \frac{\sum_{i,j}^{N} \mathbf{u}_i(\omega_n) \cdot \mathbf{u}_j(\omega_p)}{\sum^{N} |\mathbf{u}_i(\omega_p) \cdot \mathbf{u}_j(\omega_p)|}$$



4th part - IR spectrum

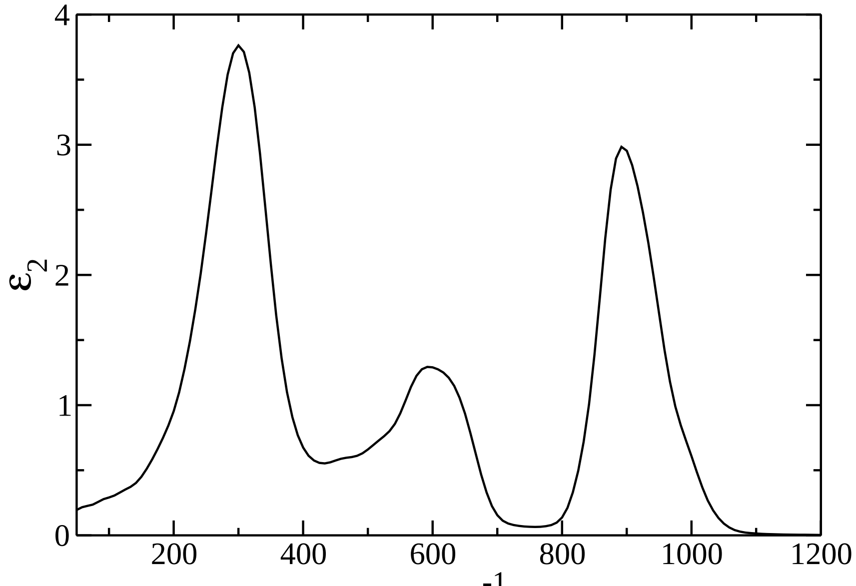
Classical MD - computation using time correlation functions

Dielectric function:

$$\epsilon(\omega) - \epsilon_\infty = \frac{\beta}{3\epsilon_0 V} \left[\langle \vec{M}(0)^2 \rangle + 2\pi\imath\omega \langle \vec{M}\cdot\vec{M}\rangle_\omega + 2\langle \vec{M}\cdot\vec{J}\rangle_\omega + \frac{\imath}{2\pi\omega}\langle \vec{J}\cdot\vec{J}\rangle_\omega \right]$$

$\langle \vec{J}\cdot\vec{J}\rangle_\omega = \int_0^\infty e^{2\pi\imath\omega t}\langle \vec{J}(t)\cdot\vec{J}(0)\rangle \mathrm{d}t$, $\vec{J}(t) = \sum_i q^i \vec{v}^i(t)$, - charge current

$\vec{M}(t) = \sum_i \vec{\mu}^i(t)$- total induced dipole moment



GeO$_2$ glass - $\epsilon_2 = \mathrm{Im}\,\epsilon$

Classical MD, DIPPIM potential (DIPole Polarizable Ion Model)

Marrocchelli, Salanne et al., Molec. Phys. **107** (2009)]

IR spectrum - from ab initio data

Formalism [Resta, Rev. Mod. Phys. **66** (1994), Pasquarello & Car, PRL **79** (1997), Umari, PhD thesis (2003)] :

- High frequency dielectric tensor : $(\epsilon_\infty)_{ij} = \delta_{ij} + 4\pi \frac{\partial^2 E_{tot}}{\partial \mathcal{E}_i \partial \mathcal{E}_j}$
- Born effective charges $Z^*_{I,jk} = -\frac{\partial^2 E_{tot}}{\partial r_{Ij} \partial \mathcal{E}_k} \equiv \frac{\partial F_{Ij}}{\partial \mathcal{E}_k}$
- Real part of the of dielectric function $\epsilon(\omega)$:

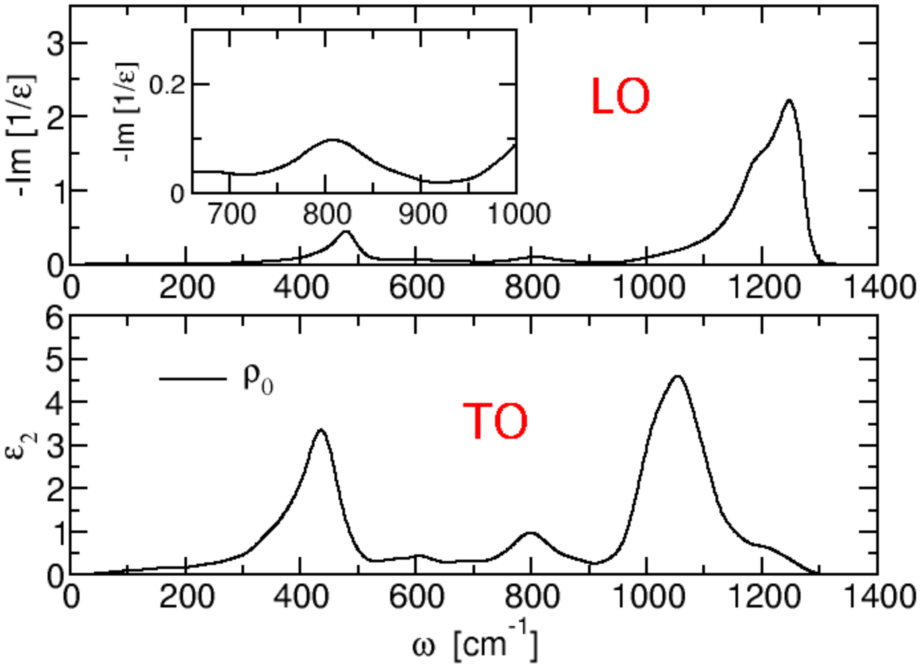
  $$\epsilon_1(\omega) = \epsilon_\infty - \frac{4\pi}{V} \sum_n \frac{|\mathcal{F}^n|^2}{\omega^2 - \omega_n^2}$$
- Imaginary part of the of dielectric function $\epsilon(\omega)$:

  $$\epsilon_2(\omega) = \frac{4\pi^2}{V} \sum_n \frac{|\mathcal{F}^n|^2}{2\omega_n} \delta(\omega - \omega_n)$$

  where $\epsilon_\infty = \mathrm{Tr}(\epsilon_\infty)_{ij}/3$ and $\mathcal{F}^n_j = \sum_{I,k} Z^*_{I,jk} \frac{e^n_{Ik}}{\sqrt{M_I}}$

IR spectrum - from ab initio data (2)

SiO_2 glass, *ab initio* approach [Matsubara, Ispas, Kob (to be submitted)]



	Theor.[cm^{-1}]	Exp.[cm^{-1}]
TO_1	435	457
LO_1	479	501
TO_2	800	810
LO_2	811	820
TO_3	1054	1076
LO_3	1246	1256

Exp. Kirk, Phys. Rev. B (1988)

- Main bands in ϵ_2 and $-\mathrm{Im}(1/\epsilon)$: overall well described with errors at most $\approx 30\mathrm{cm}^{-1}$ and good agreement to previous calculations [Umari & Pasquarello (2005), Giacomazzi et al. (2009)]

5th part - Raman spectrum

- Nonresonant Stokes Raman spectra :

$$I_k \propto |\mathrm{e}_{inc} \overset{\leftrightarrow}{\alpha}^k \mathrm{e}_{scatt}|^2 \frac{n_B(\omega_k)+1}{\omega_k}$$

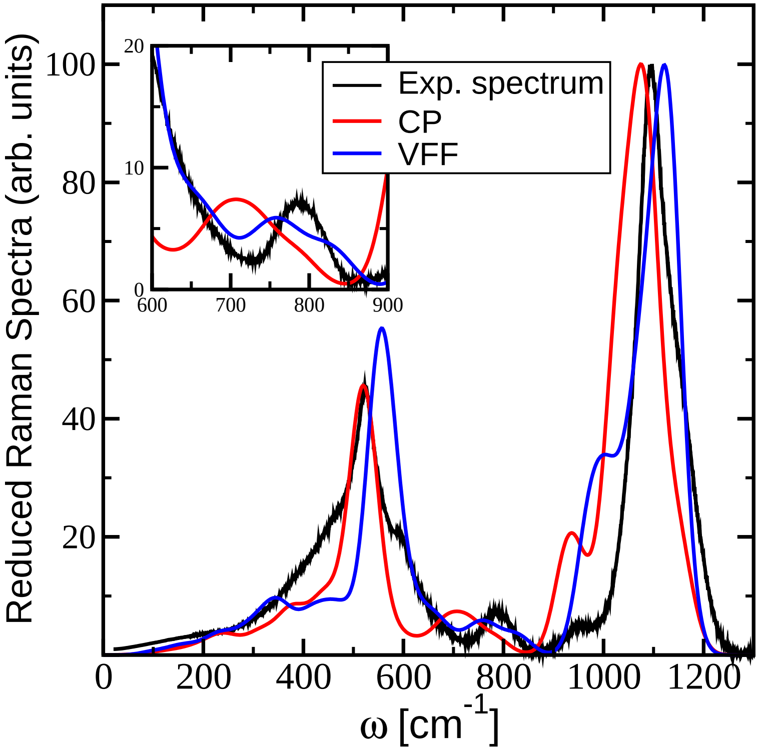
  where

$$\alpha_{ij}^k = \sum_{lm} \frac{\partial^3 E_{tot}}{\partial \mathcal{E}_i \partial \mathcal{E}_k \partial u_{lm}} \frac{e_{lm}^k}{\sqrt{M_m}}$$

- Models for computing polarizabilities ($\partial^2 E_{tot}/\partial \mathcal{E}_i \partial \mathcal{E}_k$) and its derivatives :
  - Bond polarizability (BP) model : the polarizabilities is modeled in terms of bond contributions [Alben et al, PRB **11** (1975); N. Zotov et al, PRB **60** (1999), Rahmani et al. PRB **68** (2003)]
  - Direct calculation as 2nd order derivatives of the total energy with respect to the applied electric fields [Umari & Pasquarello PRL **89** (2002), Lazzeri & Mauri PRL **90** (2003)]

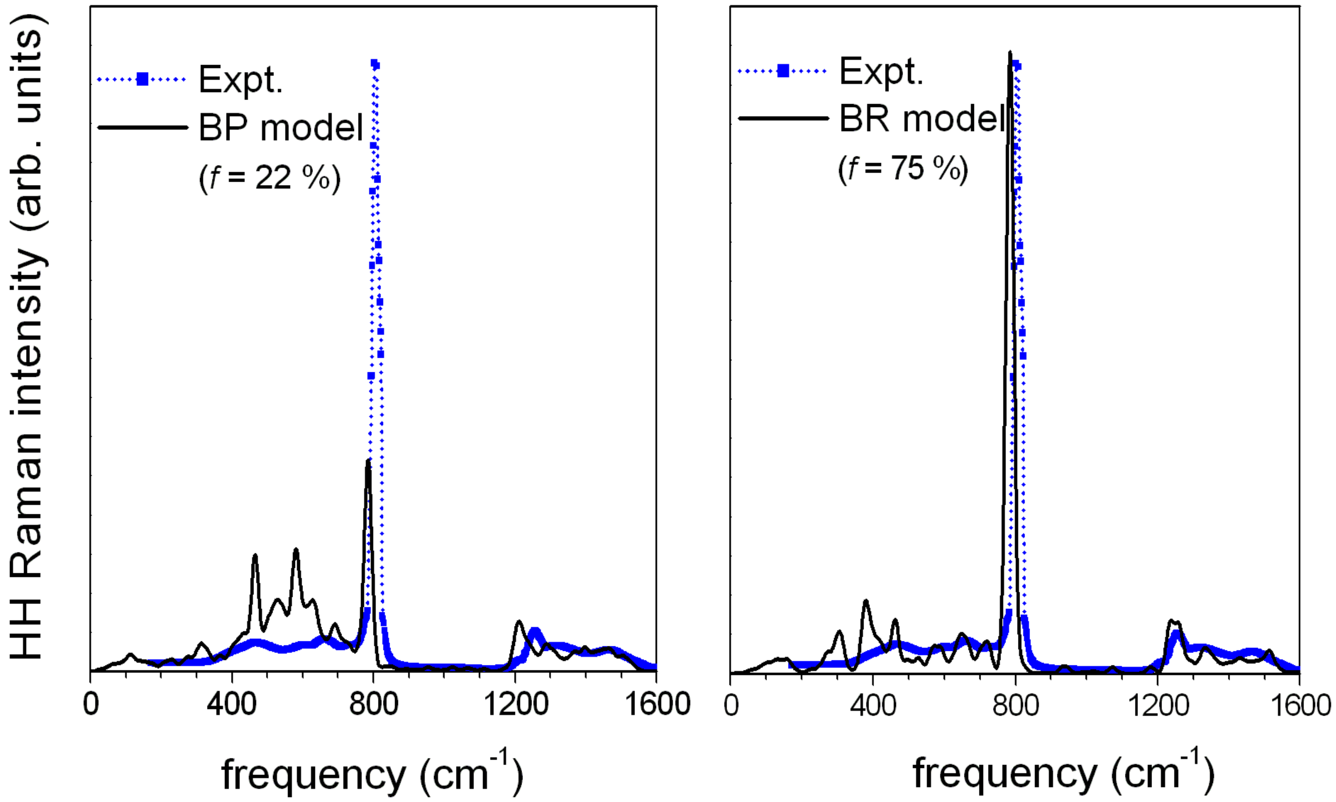
5th part - Raman spectrum (2)

- NS4 glass, BP model - Ispas et al. JNCS (2005), using two sets of $\{\omega^n, \mathbf{e}^n\}_{n=1,\ldots,3N}$, CP and VFF



5th part - Raman spectrum (3)

- B_2O_3 glass, *ab initio* approach - Ferlat, Charpentier et al. PRL (2008)
- Raman peak at $\approx$ 800 cm^{-1} : probe of the fraction f of Boroxol rings



Summary

- Nowdays atomistic simulations may generate reliable structural models for simple glasses
- Calculations of the vibrational properties of the structural models and confrontation to experimental results
- Some thermodynamical properties can be computed, e.g. specific heat
- The detailed analysis of the nature of the vibrational excitations may help to getting better insights into the relations of the local structure (bonding angles, distance, ...) with the experimental vibrational spectra