Ab Initio Molecular Dynamics Simulations in Liquids and Glasses
Basics and Applications - II

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Outline - Application to Liquids and Glasses

1 A case study : Binary Chalcogenides
  Effect of the electronic model
  Thermal history effects
  Structure and Dynamics

2 Properties from the electronic treatment
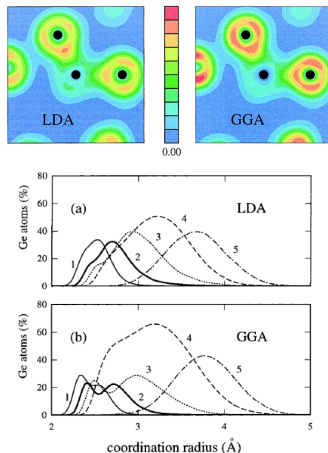 Infrared spectrum
  Raman scattering
  Electronic density of states

A case study : Binary Chalcogenides

EFFECT OF THE ELECTRONIC MODEL

Massobrio, Pasquarello and Car, JACS 121 (1999)

Nature of chemical bonding :

- In chalcogenides (e.g. $GeSe_2$ or GeS_2), presence of homopolar defects.

- Charge transfer. From covalent character to metallic. Change with temperature.

- From LDA to GGA :
  - Depletion of Ge valence charge and charge accumulation around Se indicates ionic character of the bonding. Lobes $\rightarrow$ covalent contribution to the bonding character. Increased ionic character with GGA

  - 50% (LDA) and 63% (GGA) Ge are 4-fold in l-$GeSe_2$. Too high metallic character.

Figure 3. Average Se-coordination of Ge atoms in liquid $GeSe_2$ as a function of the radius of the coordination sphere in the (a) LDA and (b) GGA. The coordination is defined as the number of nearest neighbors in the coordination sphere.
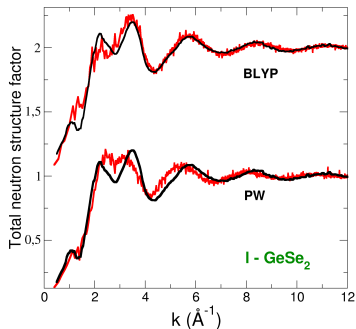
A case study : Binary Chalcogenides

EFFECT OF THE ELECTRONIC MODEL

Effect of the XC functional :

- In l-GeSe$_2$, increase of the pseudo-gap between C and V band when moving from PW (metallic character, electron gas) to BLYP (fitted on molecules).

- Increases the Ge tetrahedral coordination number and 2-fold for Se. Decrease the number of CN defects.

- Increases the number of Ge-Ge and Se-Se homopolar bondings. Increased structuration.

EFFECT OF THE ELECTRONIC MODEL

Effect of the XC functional + dispersion :

Bouzid et al. PRB 92 (2015)

- In a-GeTe$_4$, similar features on structure encoutered.

- BLYP favors a tetrahedral network, in contrast with PBE (octahedral+tetrahedral Ge).

- Dispersion corrections (VdW) cure a so-called Ge-Te "*bond distance problem*".

$$E_{disp} = -s_6 \sum_i \sum_j \frac{C_{ij}}{R_{ij}^6} f_{damp}(R_{ij})$$
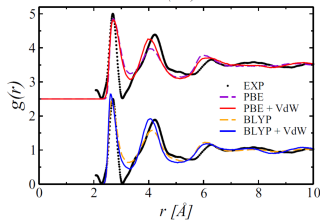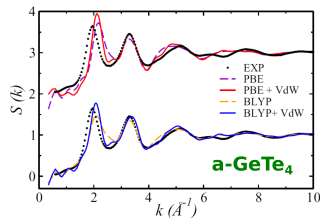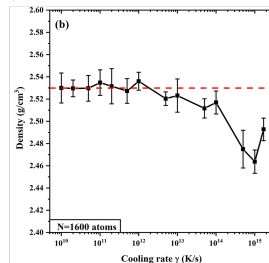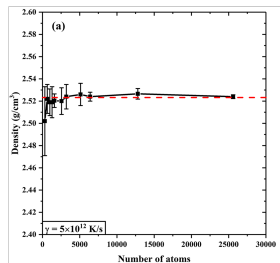
A case study : Binary Chalcogenides

THERMAL HISTORY EFFECTS

- Effects of system size (10^7) and cooling rate of the simulation process (10^8 K/s-10^{15} K/s) in classical MD simulations are well known and documented

- Properties depend on the thermal history.

- Effects even more problematic in ab initio MD.
    - N=100-1000 atoms, 100 ps, 10^{13}-10^{16} K/ps

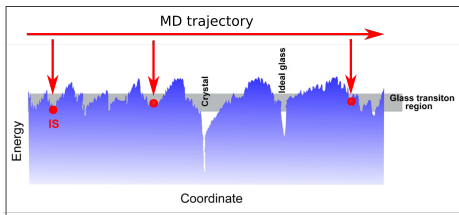   - N=480 glassy GeSe$_2$, 350 ps
   → 56 years single CPU !!!

THERMAL HISTORY EFFECTS
Averages over inherent structures

C. Yildirim, PhD Thesis (2017)

$Ge_{22}Se_{78}$

- Liquids visit many configurations prior to 10-100 K/ps quenching followed by structural relaxation

- Produce independent quenches to generate inherent structures (local minima of the potential energy landscape)
- Average the glass structures for reliable results
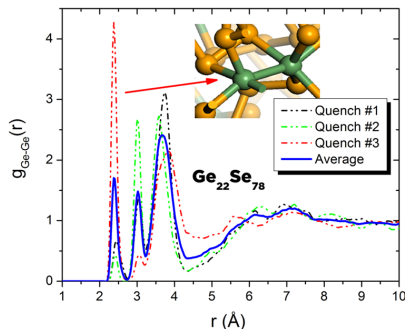
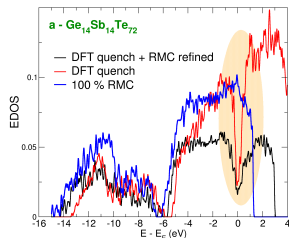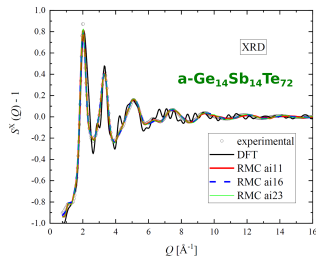# A case study : Binary Chalcogenides

THERMAL HISTORY EFFECTS

Are there alternatives for saving time ?

1. Reverse Monte Carlo
   - Glass configuration prepared by RMC. Then, DFT investigation.

   - **Pros:** Time saving. Increased match with experimental structure (?).
     Cons: Unphysical model structure without relaxation events during the quenching (energy barriers).

   - RMC refinment : DFT quench to 300 K$\rightarrow$ RMC$\rightarrow$ DFT investigation.

2. Classical MD prior to DFT study
   - Valid for oxides. But for chalcogenides ?

$S^X(Q) - 1$ vs Q [Å^{-1}], XRD, a-Ge$_{14}$Sb$_{14}$Te$_{72}$

- experimental
- DFT
- RMC ai11
- RMC ai16
- RMC ai23

a - Ge$_{14}$Sb$_{14}$Te$_{72}$, EDOS vs E - E$_F$ (eV)

- DFT quench + RMC refined
- DFT quench
- 100 % RMC

A case study : Binary Chalcogenides

STRUCTURE AND DYNAMICS

1. **Ge_xSe_{1-x}, As_xSe_{1-x} or Ge_xS_{1-x}**
   - Accurate glass structures, in excellent agreement with scattering experiments.

   - Presence of homopolar defects (Ge-Ge, As-As, Se-Se, S-S).
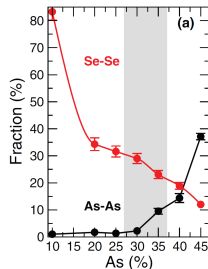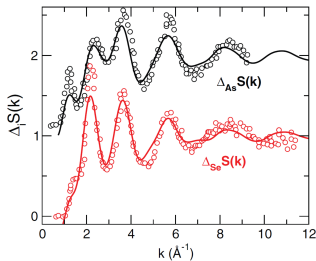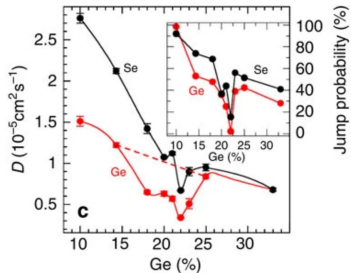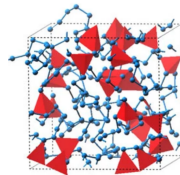
A case study : Binary Chalcogenides

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A case study : Binary Chalcogenides

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2. **Densified chalcogenides**
   - Coordination and geometry change with pressure
   - Evidence of polyamorphism

Properties from the electronic treatment
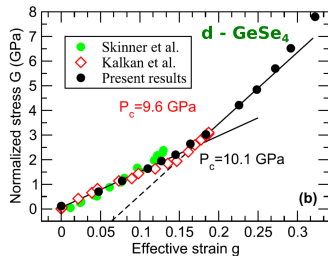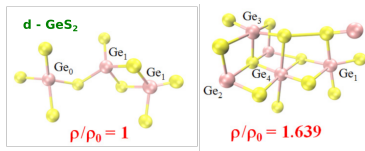
INFRARED SPECTRUM

Different methods can be used:

1. **Finite electric field (ϵ) method** (Umari and Pasquarello, PRL 89 (2002))
   - One adds into the functional a term $E_{ion} = -\boldsymbol{\epsilon}.\mathbf{P}_{ion}$ with

   $$\mathbf{P}_{ion} = \sum_i Z_i.\mathbf{R}_i$$

   - Dynamic Born charge tensors $Z^* = F_\epsilon/\epsilon$ give acces to IR spectrum.

2. **Linear response theory** (DFT perturbation theory, Putrino and Parrinello, PRL 2002)
   - Similarly to the calculation of e.g. transport coefficients in linear response theory (autocorrelation functions)
   - One considers consider the response of the system under a small perturbation through response (Green) functions coupled to an excitation at frequency ω.

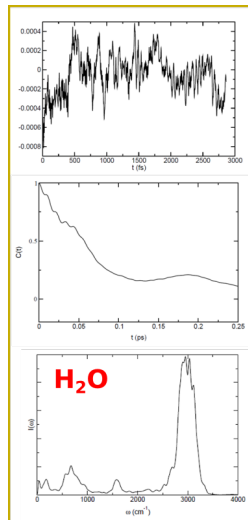# Properties from the electronic treatment

INFRARED SPECTRUM

- Perturbation to the Hamiltonian is : $-\mathbf{M}.\mathbf{E}$ with $\mathbf{M}$ the dipolar momentum.

- Using linear response theory, one can show that the infrared absorption is :

$$\epsilon_2(\omega) = \frac{2\pi}{3Vk_BT} \int\limits_{-\infty}^{\infty} e^{-i\omega t} \langle \mathbf{M}(t).\mathbf{M}(0)\rangle \, dt$$
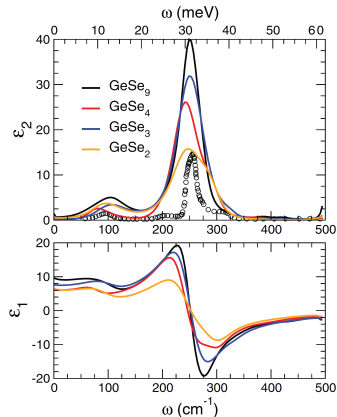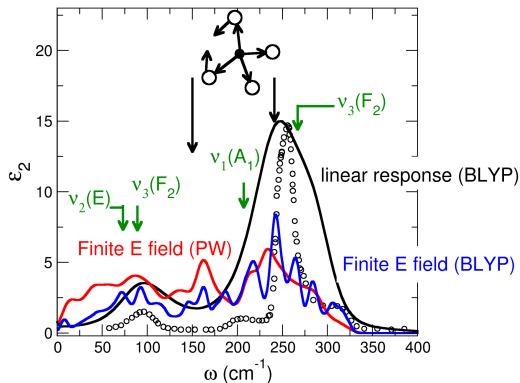
- Real part from Kramers-Krönig relations:

$$\epsilon_1(\omega) = \frac{2}{\pi} \int\limits_{0}^{\infty} \frac{\Omega\epsilon_2(\Omega)}{\Omega^2 - \omega^2} d\Omega$$
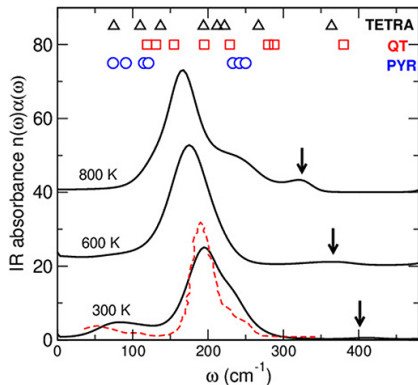

H$_2$O

INFRARED SPECTRUM of Ge-Se GLASSES
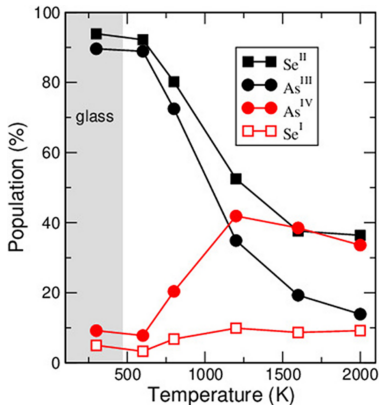
M. Micoulaut et al. PRB 88 (2013)

Properties from the electronic treatment

INFRARED ANALYSIS OF As$_2$Se$_3$

Signatures of coordination defects can be decoded from the analysis of the infrared spectra of liquid and glassy As$_2$Se$_3$.
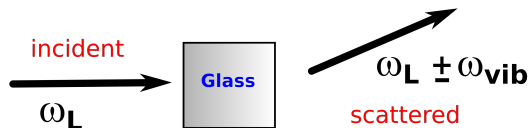

Presence of a defect line at 350-400 cm^{-1} compatible with the presence of four-fold As

Properties from the electronic treatment

RAMAN SCATTERING

Polarisation induced by electric field $\mathbf{E}$: $\mathbf{M} = \overset{\leftrightarrow}{\chi}\, \mathbf{E}(t) = \overset{\leftrightarrow}{\chi}\, \mathbf{E}_m \cos \omega_L t$

$$\overset{\leftrightarrow}{\chi}(\{R\}) = \overset{\leftrightarrow}{\chi}(\{R_0\}) + \left(\{R\} - \{R_0\}\right) \frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \{R\}} + ...$$

Harmonic approximation of the lattice dynamics: $\{\mathbf{R}\} - \{\mathbf{R}_0\} \simeq u \cos \omega_{vib} t$

$$\mathbf{M} = \overset{\leftrightarrow}{\chi}(\{R_0\})\mathbf{E} \cos \omega_L t + \frac{1}{2} \frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \{R\}} \mathbf{E}_m u \left[\cos(\omega_L + \omega_{vib})t + \cos(\omega_L - \omega_{vib})t \right]$$

RAMAN SCATTERING

Raman cross section

$$\frac{d\sigma}{d\Omega} \propto V\left(\frac{\omega_L}{c}\right)^4 \sum_{vib} \left| \mathbf{e}_s \cdot \frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \{Q_{vib}\}} \cdot \mathbf{e}_L \right|^2 \frac{\hbar}{2\omega_{vib}} \cdot A_{vib}$$

with Raman susceptibility :

$$\frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \{Q_{vib}\}} = \sum_I \frac{\mathbf{e}^I_{vib}}{\sqrt{M_I}} \cdot \frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \mathbf{R}_I}$$

and Raman tensor :

$$\frac{\partial \overset{\leftrightarrow}{\chi}}{\partial \mathbf{R}_I} = \frac{\partial \chi_{\mu\nu}}{\partial \mathbf{R}_I} \propto \frac{\partial^2 F_I}{\partial E_\mu \partial E_\nu}$$
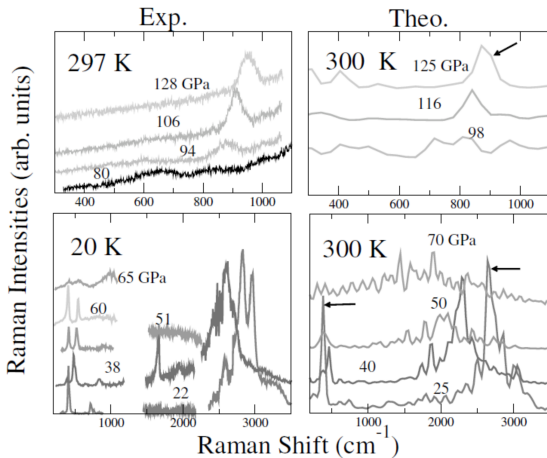
Alternative : Linear response theory from polarizability tensor :

$$\overset{\leftrightarrow}{\alpha} = \alpha_{\mu\nu}(t) = -\frac{\partial \mathbf{P}_\mu}{\partial \mathbf{E}_\nu} \equiv \frac{\partial^2 E}{\partial \mathbf{E}_\mu \partial \mathbf{E}_\nu}$$

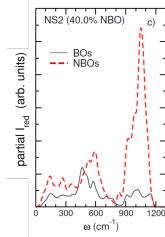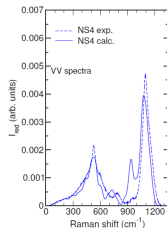# Properties from the electronic treatment

RAMAN SCATTERING

RAMAN SCATTERING

- Excellent reproduction of the Raman spectra

- Sodium silicates: Atomic scale contribution or contribution of identified species

- Beyond experimental Gaussian deconvolution

- More details: P. Giannozzi et al., JPCM 21 (2009)
  http://www.quantum-espresso.org

ELECTRONIC DENSITY OF STATES

Micoulaut et al. PRB 104 (2021)

- Computation of the KS eigenstates allows to obtain electronic density of states.

- Directly comparable with experiments from X-ray photoemission spectroscopy (XPS) for the valence band and with inverse photoemission for the conduction band.
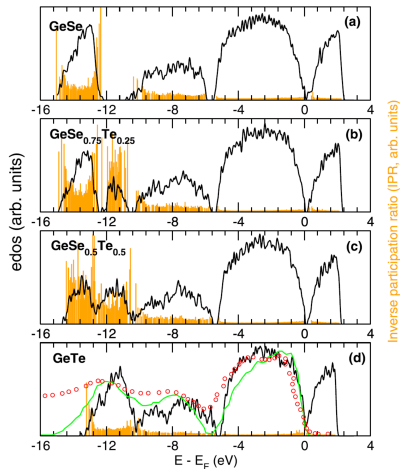
ELECTRONIC DENSITY OF STATES

Prasai and Drabold, PRB 83 (2011)

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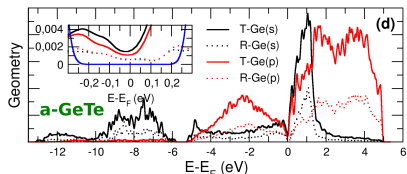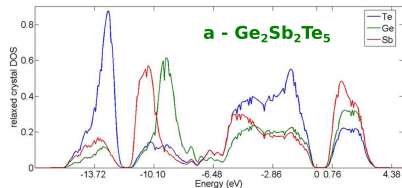
- Details from atomic structure (species, coordination defects,...) provides insight.

a - $Ge_2Sb_2Te_5$

a-GeTe

Micoulaut and Flores-Ruiz, (2022)

Conclusion

- Ab initio methodology well established for glasses and liquids.

- Access to structure and dynamics ($\propto$ classical MD) for covalent and semi-metallic systems.

- New properties can be calculated from ab initio simulations (Raman, IR, XPS, ...) in order to establish structure-property relationships.

- Atomic scale insight into vibrational spectra

- Possibility to investigate properties of chalcogenides or densified glasses

- Applications in optoelectronics where electronic phenomena are clearly at play.

Merci à : Steve Martin, Jincheng Du