Interprétation avancée des calculs premiers principes des phonons par SIESTA

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Modélisation au sein de LCP-AM2C: périmètre, noms et chiffres

Laboratoire de Chimie et Physique – Approche Multi-Echelles des Milieux Complexes, résultant de la fusion (janvier 2012) des ex-laboratoires/équipes suivantes:

- Equipe Biophysique Statistique du LPMC (Laboratoire de Physique Moléculaire et Collisions);
- LPMD (Laboratoire de Physique des Milieux Denses);
- LSMCL (Laboratoire de Spectrométrie de Masse et Chimie Laser);
- LCME (Laboratoire de Chimie et Méthodologie pour l'Environnement).

Thèmes principaux de la recherche:

'1) 'Ordre-désordre/auto-organisation' (Rhéophysique des colloïdes, désordre d'alliage dans les systèmes atomiques);

2) 'Chimie durable et environnement'
(Contaminants et Dépollution, gestion durable des ressources).

46 enseignants-chercheurs sur les sites de Metz (Institut de Chimie et Physique, 1 Bd Arago, Technopôle) et Saint-Avold (IUT de Moselle-Est).

Michaël BADAWI

✴Chimie quantique, adsorption, catalyse, surfaces, sureté nucléaire

Logiciels commerciaux pour calculs ab initio:
VASP (structures periodiques);
Gaussian (moléculaires)

Effect of water on the stability of Mo and CoMo hydrodeoxygenation catalysts: A combined experimental and DFT study

M. Badawi[a], J.F. Paul[a], S. Cristol[a], E. Payen[a], Y. Romero[b], F. Richard[b], S. Brunet[b], D. Lambert[c], X. Portier[d],
A. Popov[e], E. Kondratieva[e], J.M. Goupil[e], J. El Fallah[e], J.P. Gilson[e], L. Mariey[e], A. Travert[e,*], F. Maugé[e]

[a] Unité de Catalyse et Chimie du Solide, Université de Sciences et Technologie de Lille, CNRS, 59650 Villeneuve d'Ascq, France
[b] Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, CNRS, 40, avenue du Recteur Pineau, 86022 Poitiers, France
[c] Total Petrochemicals Research Feluy, Zone Industrielle C, B-7181 FELUY, Belgium
[d] CIMAP, ENSICAEN, Université de Caen, CNRS, CEA, 6, Boulevard du Maréchal Juin, 14050 Caen, France
[e] Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6, Boulevard du Maréchal Juin, 14050 Caen, France
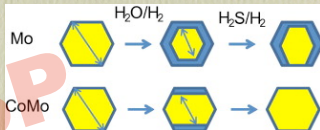
Highlights
► Impact of H₂O on Mo and CoMo sulfide catalysts during HDO of phenolic compounds.
► Non-promoted Mo catalysts are more sensitive   toward water due to SO exchanges.
► Co improves the activity (promotion) and stability of the active phase (passivation).

Ab initio calculations and iodine kinetic modeling in the reactor coolant system of a pressurized water reactor in case of severe nuclear accident

Bertrand Xerri[a,c], Sébastien Canneaux[b,c], Florent Louis[b,c,*], Julien Trincal[c], Frédéric Cousin[a,c],
Michael Badawi[a,c], Laurent Cantrel[a,c,*]

[a] Institut de Radioprotection et de Sûreté Nucléaire, DPAM/SEMIC, Centre de Cadarache, BP3, 13115 Saint Paul Lez Durance Cedex, France
[b] PhysicoChimie des Processus de Combustion et de l'Atmosphère (PC2A), UMR 8522 CNRS/Lille1, Université Lille 1 Sciences et Technologies, Cité scientifique, Bât C11/C5, 59655
Villeneuve d'Ascq Cedex, France
[c] Laboratoire de Recherche Commun IRSN-CNRS-Lille1 "Cinétique Chimique, Combustion, Réactivité" (C³R), Centre de Cadarache, BP3, 13115 Saint Paul Lez Durance Cedex, France

Highlights
► Thermodynamic and kinetic parameters are calculated using ab initio molecular orbital methods.
► Calculated reaction enthalpies at 0 K are close to their literature counterparts.
► Rate constants are calculated from 300 to 2500 K and compared to the available literature data.
► Iodine kinetic model is developed.
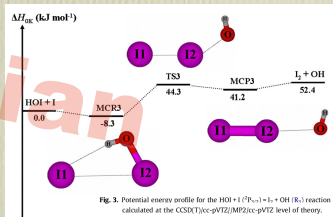► Simulations with the ASTEC software are performed in the framework of nuclear safety.

Fig. 3. Potential energy profile for the HOI + I (²P₃/₂) = I₂ + OH (²Π₃/₂) reaction calculated at the CCSD(T)/cc-pVTZ//MP2/cc-pVTZ level of theory.

Jean-Marc BOMONT

- Relation structure moléculaire – propriétés macroscopiques: les gaz rares etc.
- Etude de colloïdes (dynamique moléculaire, Monte-Carlo), de la thermodynamique statistique et de la méthode des équations intégrales auto-cohérentes.
- Propriétés optiques non-linéaires de fluides simples.
- Simulation hors équilibre (NEMD).
- Développement de potentiels interatomiques analytiques de métaux liquides (Hg).

Logiciels utilisés "maison" (Fortran 77 ou 90, sequentiels): Dynamique moléculaire classique; Monte Carlo
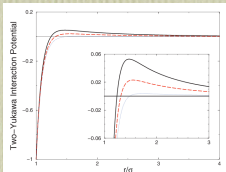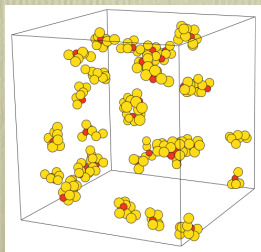

FIG. 1. The 2Y interaction potential. Full line: $K_2/K_1 = 0.1$; dashed line: $K_2/K_1 = 0.05$; dotted line: $K_2/K_1 = 0.01$. All potentials are rescaled in such a way that the depth of the potential well $u = K_1 - K_2$ is equal to minus one. The inset contains a magnification of the region around the repulsive barrier.

Temperature study of cluster formation in two-Yukawa fluids

Jean-Marc Bomont,[1,a] Jean-Louis Bretonnet,[1] and Dino Costa[2]

[1]Laboratoire de Physique des Milieux Denses, Université de Metz, 1 Bd. Arago, 57 078 Metz, France
[2]Dipartimento di Fisica, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

INVITED ARTICLE

Theoretical description of cluster formation in two-Yukawa competing fluids

D. Costa[a]*, C. Caccamo[a], J.-M. Bomont[b] and J.-L. Bretonnet[b]

[a]Dipartimento di Fisica, Università degli Studi di Messina, Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy;
[b]Laboratoire de Physique des Milieux Denses, Université Paul Verlaine, 1 Bd. Arago, 57070 Metz, France

Snapshot of an equilibrated sample at $T^* = 0.46$ with $K_2/K_1 = 0.10$.
For the clarity sake, only particles involved in the formation of clusters are shown. Red particles represent the seeds of the compact structures.

Réné MESSINA
✳ Cristallisation de colloïdes chargés binaires

Logiciels utilisés "maison" (Fortran 77 ou 90, sequentiels)
pour faire :
• Monte Carlo
• Dynamique brownienne ou de Langevin (équilibre & hors équilibre)
• Minimisation d'énergie sur réseaux cristallins
• Résolution d'équations différentielles non linéaires (Poisson-Boltzmann)

Configuration "idéale" du calcul: 40-50 nœuds; 1 Go RAM / CPU

Ionic mixtures in two dimensions: From regular to empty crystals

L. ASSOUD, R. MESSINA and H. LÖWEN

Institut für Theoretische Physik II: Weiche Materie, Heinrich-Heine-Universität Düsseldorf
Universitätsstrasse 1, D-40225 Düsseldorf, Germany, EU

Fig. 3: (Colour on-line) Stable structures of oppositely charged spheres *vs.* their size asymmetry $\sigma = R_B/R_A$ in the substrate model, where all sphere surfaces touch the same plane: a) side view, b) (scaled) energy per ion. Discontinuous transitions between the structures are indicated by a solid bar. Continuous transitions are denoted by a broken bar. Bottom views of the unit cells of the corresponding stable phases are displayed, where the big (small) spheres have a radius R_A (R_B).
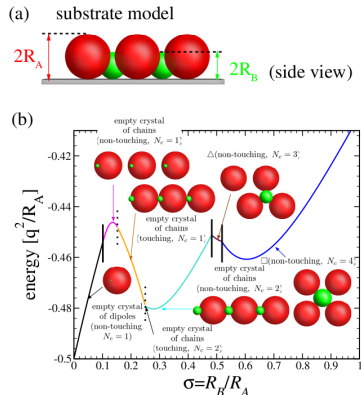
Martin Mickaël MULLER

✳ Propriétés géometriques des membranes biologiques

Codes open source: libMesh (mesh support),
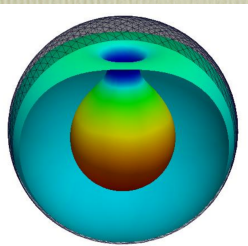VTK (visualisation), OpenMPI

Morphogenesis of membrane invaginations in spherical confinement

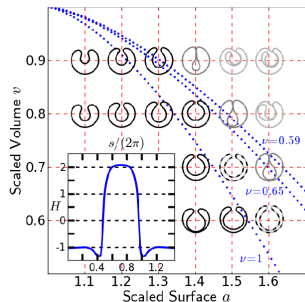O. KAHRAMAN[1], N. STOOP[2] and M. M. MÜLLER[1]

[1] Equipe BioPhysStat, ICPMB-FR CNRS 2843, Université de Lorraine - 1, boulevard Arago,
F-57070 Metz, France, EU
[2] Computational Physics for Engineering Materials, ETH Zurich - Schafmattstr. 6, HIF,
CH-8093 Zurich, Switzerland

a geometrical phase diagram
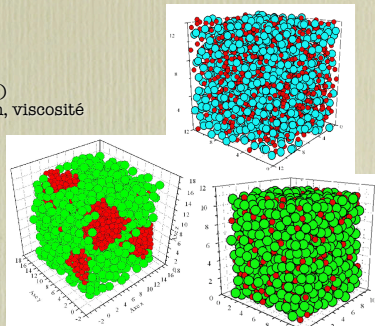of fluid membrane invaginations:

Numerical equilibrium solution for a
membrane (smooth surface) inside a spherical container (black
mesh) with scaled area $a = 1.2$ and scaled volume $v = 0.8$. The
membrane bulges inward and forms an invagination reminiscent of a light bulb.

Jean-François WAX

- Dynamique des liquides (surtout des métaux)
- Propriétés statiques et dynamiques, diffusion, viscosité
- Digrammes de phase densité - température

Dynamique Moléculaire classique
(code maison) et ab initio (VASP)

Multiscale study of the influence of chemical order on the properties of liquid Li-Bi alloys

J.-F. Wax
Laboratoire de Physique des Milieux Denses, Université Paul Verlaine - Metz, 1, Boulevard F. D. Arago, F-57078 Metz Cedes 3, France

M. R. Johnson
Institut Laue Langevin, 6 rue Jules Horowitz, F-38042 Grenoble Cedex 9, France

L. E. Bove
Physique des Milieux Denses, IMPMC, CNRS-UMR 7590, Université Pierre et Marie Curie, F-75252 Paris, France

M. Mihalković
Institute of Physics, Slovak Academy of Sciences, Dubravska cesta 9, 84511 Bratislava, Slovakia

L'ordre chimique dans un liquide:
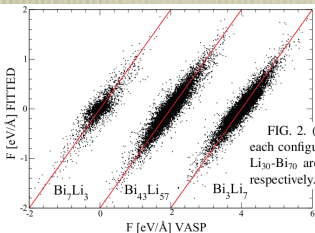aléatoire; homocoordonné; hétérocoordonné...

→ Paramètrisation
de la DM classique

FIG. 2. (Color online) Fitted forces versus *ab initio* ones for each configuration considered. Data corresponding to Li$_{57}$-Bi$_{43}$ and Li$_{30}$-Bi$_{70}$ are shifted by 2 and 4 eV/Å along the horizontal axis, respectively.
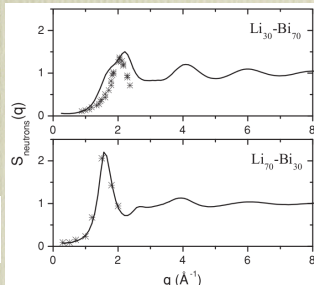
FIG. 6. Total structure factors for neutrons (full line: simulation; symbols: experiment).

Hong XU

- Dynamique moléculaire classique et ab initio des liquides complexes
- Transitions de phase dans des liquides; propriétés interfaciales

Logiciels utilisés "maison" et
LAMMPS (C++, MPI)

Structure and dynamics of cylindrical micelles at equilibrium and under shear flow

C.-C. Huang,[1] J.-P. Ryckaert,[2] and H. Xu[3]

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[2]Physique des Polymères, Université Libre de Bruxelles, Campus Plaine, CP 223, B-1050 Brussels, Belgium
[3]Laboratoire de Physique des Milieux Denses, Université Paul Verlaine–Metz, 1 Boulevard Arago, 57078 Metz Cedex 3, France
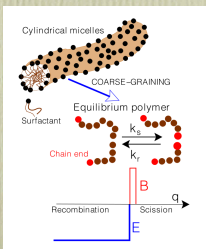(Received 28 November 2008; published 9 April 2009)

FIG. 8. (Color online) The extinction angle χ_O vs β_Λ and vs $\dot{\gamma}$ (inset), for both semidilute cases. Data correspond to $W=12$, with $\omega=0.02$ (cross), $\omega=0.1$ (down triangles), $\omega=1$ (stars); and $W=10$ with $\omega=0.1$ (filled circles), $\omega=0.5$ (open squares), $\omega=1$ (up triangles), $\omega=5$ (open diamonds). The continuous line in the main figure corresponds to the empirical law.
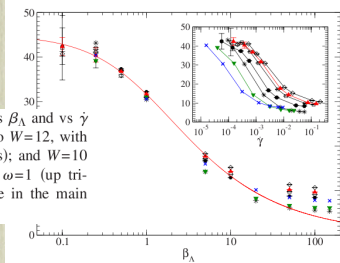

Figure 1: Some surfactant molecules in solution self-assemble and form long wormlike micelles which continuously break and recombine. Their mass distribution is, hence, in thermal equilibrium and they present an important example of the vast class of systems termed "equilibrium polymers"[1].

Andrei POSTNIKOV

- Structure électronique ab initio (DFT): solides, liquides, molécules
- Dynamique de réseau des semiconducteurs mixtes

Logiciels utilisés:
- SIESTA (pseudopotentiels, fonctions de base numériques)
- WIEN2k ("tous électrons")

~10^2 - 10^3 atomes, periodiques ou isolés (SIESTA)

Impurity vibration modes
in II–VI and III–V mixed semiconductors

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Laboratoire de Physique des Milieux Denses, Paul Verlaine University, 1 Bd Arago, 57078 Metz, France

ELSEVIER

Review

STM spectroscopy of magnetic molecules

K. Petukhov[a], M.S. Alam[a], H. Rupp[a], S. Strömsdörfer[a], P. Müller[a,*], A. Scheurer[b],
R.W. Saalfrank[b], J. Kortus[c], A. Postnikov[d], M. Ruben[e], L.K. Thompson[f], J.-M. Lehn[g]

SIESTA

Figure 4 Calculated vibration patterns in selected zone-center coupled-impurity modes. Top row: Ga (large spheres) impurities in InAs; the modes at 248 cm^{-1} and 250 cm^{-1}. Bottom row: In (large spheres) impurities in GaAs; the modes at 235 cm^{-1} and 238 cm^{-1}.
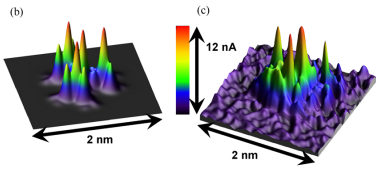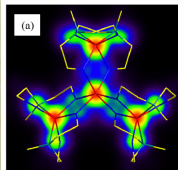
Fig. 13. (a) Color coded map of the DFT calculated electron density of **3** within an energy window between E_F and −0.95 eV in superposition with the crystal structure data (sticks), the scale is 1.2 nm × 1.2 nm. (b) 3D representation of the DFT electron density map; (c) 3D representation of the central section of the experimental CITS map taken at −0.918 V.

SIESTA way to phonons

1. $\mathbf{q} = 0$ only needed? $\rightarrow$ frozen phonons. $\quad m_\alpha \ddot{u}^i_\alpha = -\sum_\beta^N \sum_j^3 F^{ij}_{\alpha\beta} u^j_\beta$

2. Dispersion needed? $\rightarrow$ construct a supercell, look at forces induced everywhere.

3. Fourier-transform the force constants; diagonalize for any $\mathbf{q}$ needed.

$$\begin{pmatrix} \vdots \\ \dfrac{F^{ij}_{ss'}(\mathbf{q})}{\sqrt{m_s m_{s'}}} - \omega^2 \delta_{ss'} \delta_{ij} \\ \vdots \end{pmatrix} \begin{pmatrix} \vdots \\ u^j_{s'\mathbf{q}} \sqrt{m_{s'}} \\ \vdots \end{pmatrix} = 0$$

4. A case of solid solution, e.g., mixed semiconductors: supercell anyway; exact lattice periodicity is broken anyway $\rightarrow$ case 1.

5. However, a large supercell contains folded-in $\mathbf{q} \neq 0$ modes, and many "long" eigenvectors contain a lot of information. Try to extract it.

q-resolved modes density

In solid solutions, where topological disorder destroys an exact crystal periodicity, the projection of phonon eigenvectors taken along with a $\exp(i\mathbf{q}\mathbf{R})$ plane wave may help to reveal somehow a smeared $\omega(\mathbf{q})$ dispersion trends in a form of "spectral function":

$$I_{\aleph}(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \aleph} \mathbf{A}_i^{\alpha}(\omega) e^{i\mathbf{q}\mathbf{R}_\alpha} \right|^2 \delta(\omega - \omega_i).$$

It amplifies the weights of vibrations in which similar atoms move in phase with a given $\mathbf{q}$-wave throughout the crystal, and suppresses the movements whose phase are at random with such wave. In particular, the $\mathbf{q}=0$ projection amplifies the "prototype" zone-center TO mode of zincblende crystal, the quasi rigid movement of the cation sublattice against the anion one:

$$I_{\aleph}(\omega, \mathbf{q}=0) = \sum_i \left| \sum_{\alpha \in \aleph} \mathbf{A}_i^{\alpha}(\omega) \right|^2 \delta(\omega - \omega_i).$$

q-resolved modes density: an example of (Zn,Be)Se

#1 #2

- Zn
- Be
- Se
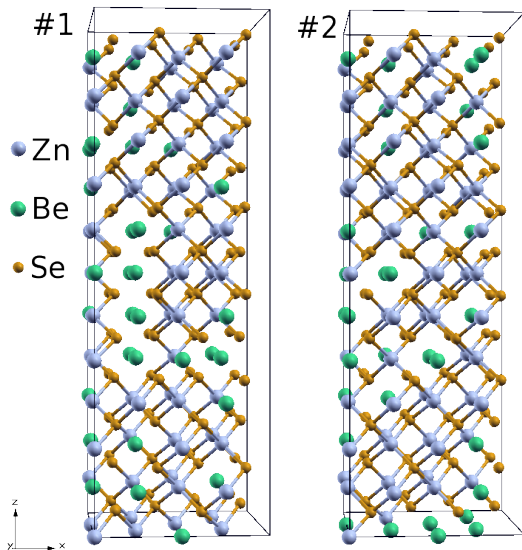
• **Motivation:**
probing the "1-bond – 2-mode" behaviour away from the Brillouin zone center.

• Solid solution is simulated by **S**pecial **Q**uasirandom **S**upercells.

• Two different ones were tried, of $64 \times 3 = 192$ atoms (long in one dimension, in order to well probe the dispersion).

• **Experimental situation:**
inelastic neutron scattering (Mala N. Rao – Tista Basak – S.L. Chaplot *et al.*); tentative synthesis by Olivier Pags (under preparation)
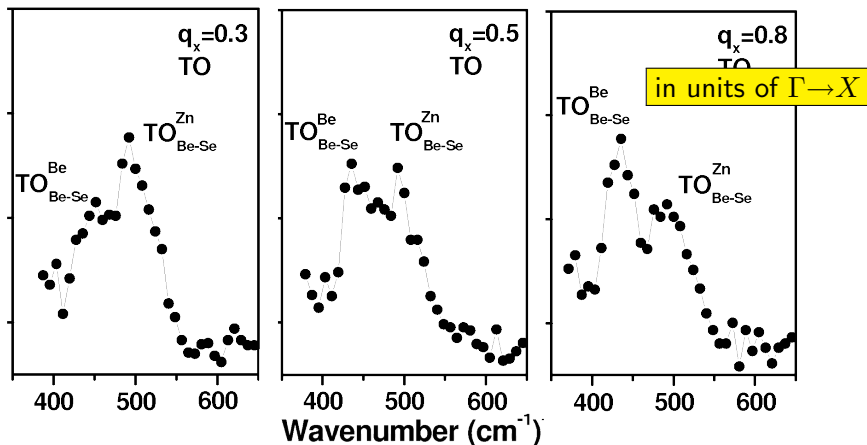
q-resolved modes density: an example of (Zn,Be)Se
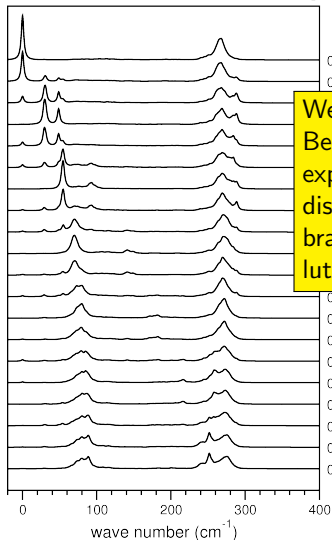
Experimental situation:
inelastic neutron scattering (Mala N. Rao – Tista Basak – S.L. Chaplot *et al.*)

We know this situation at $\mathbf{q}=0$, and assign the labels correspondingly.
Would an *ab initio* simulation confirm this?

q-resolved modes density: an example of (Zn,Be)Se

Be$_{32}$Zn$_{64}$Se$_{96}$; Zn contribution (#1)
projected vibration DOS for q = (0 0 q$_z$) q$_z$ (Bohr^{-1})

Be$_{32}$Zn$_{64}$Se$_{96}$; Be contribution (#1)
projected vibration DOS for q = (0 0 q$_z$) q$_z$ (Bohr^{-1})
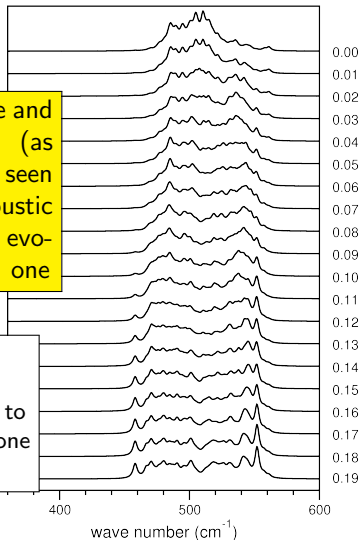
Well separated Zn-Se and Be-Se vibrations... (as expected). A clearly seen dispersion in the acoustic branch... and some evolutions in the optical one

$\leftarrow$ abs. units. The last value $\approx$ corresponds to the Brillouin zone boundary (X).

wave number (cm^{-1})

q-resolved modes density: an example of (Zn,Be)Se

Be$_{32}$Zn$_{64}$Se$_{96}$; Zn contribution (#1)
projected vibration DOS for q = (0 0 q$_z$)   q$_z$ (Bohr^{-1})
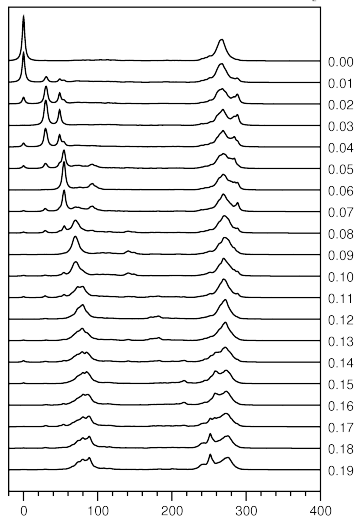
Be$_{32}$Zn$_{64}$Se$_{96}$; Zn contribution (#2)
projected vibration DOS for q = (0 0 q$_z$)   q$_z$ (Bohr^{-1})
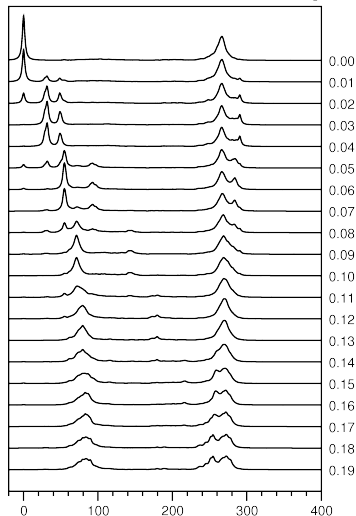
Check whether the trends depend much on the supercell... Seems not to be the case!

q-resolved modes density: an example of (Zn,Be)Se

Be$_{32}$Zn$_{64}$Se$_{96}$; Be contribution (#1)
projected vibration DOS for q = (0 0 q$_z$)   q$_z$ (Bohr^{-1})

Be$_{32}$Zn$_{64}$Se$_{96}$; Be contribution (#2)
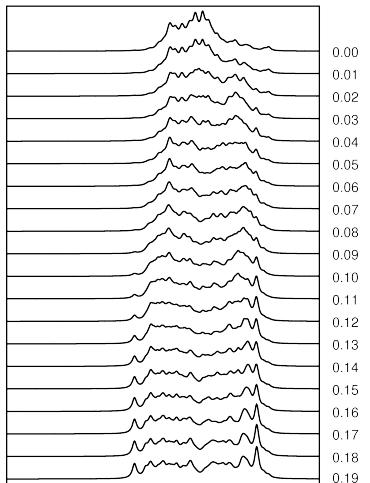projected vibration DOS for q = (0 0 q$_z$)   q$_z$ (Bohr^{-1})
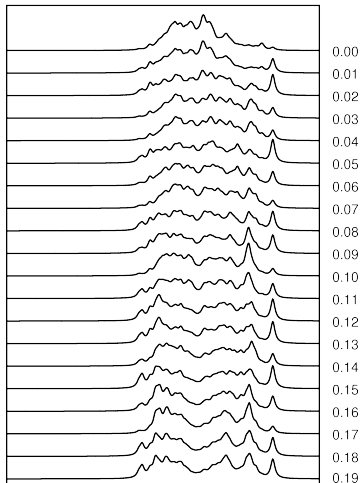
More pronounced are supercell-dependent differences in the Be-Se domain
(Be is in minority and worse "averaged"). Nevertheless, the two-mode behaviour persists.

Projecting into Longitudinal and Transversal components

$$I_{\aleph}^{\mathsf{L}}(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \aleph} \left(\frac{\mathbf{q}}{|\mathbf{q}|} \cdot \mathbf{A}_i^{\alpha} \, e^{i\mathbf{q}\mathbf{R}_{\alpha}} \right) \right|^2 \delta(\omega - \omega_i) \, ;$$

$$I_{\aleph}^{\mathsf{T}}(\omega, \mathbf{q}) = \sum_i \left| \sum_{\alpha \in \aleph} \left[\mathbf{A}_i^{\alpha} - \frac{(\mathbf{q} \cdot \mathbf{A}_i^{\alpha})}{|\mathbf{q}|} \right] e^{i\mathbf{q}\mathbf{R}_{\alpha}} \right|^2 \delta(\omega - \omega_i) \, .$$
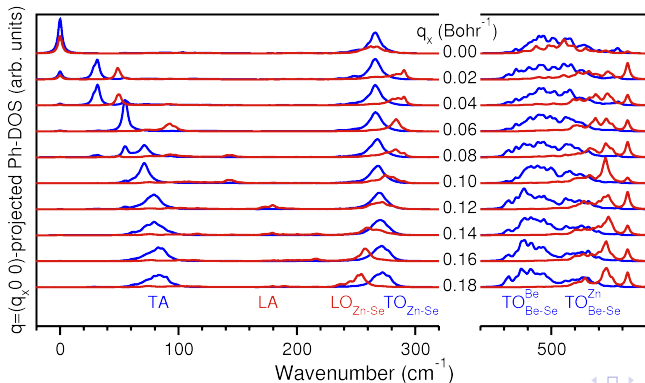
An example
of (Zn,Be)Se:

note the crossing of
LO and TO branches
with q
in the ZnSe domain.

Symmetry considerations for phonons

"Conventional" approach to symmetry of vibrations ($\rightarrow$ "frozen phonons"):
Symmetry coordinates (along to irred.rep. of the space group in question):
$S_t = \sum_j B_{tj} u_j$.   Classical kinetic and potential energy:

$$
\begin{aligned}
\mathcal{T} &= \sum_i \frac{m_i \dot{u}_i^2}{2} = \sum_{tt'i} (B^{-1})_{it} (B^{-1})_{it'} \frac{m_i}{2} \dot{S}_t \dot{S}_{t'}, \\
U &= \frac{1}{2} \sum_{tt'} F_{tt'} S_t S_{t'}.
\end{aligned}
$$

Lagrangian equation of motion:

$$
\sum_{t'} \left[\sum_i (B^{-1})_{it}\, m_i\, (B^{-1})_{it'} \ddot{S}_{t'} + (F_{tt'} + F_{t't}) S_{t'} \right] = 0
$$

with $G_{tt'} = \sum_i B_{it} m_i^{-1} B_{it'}$ – kinetic energy matrix

$$
\left[\mathbf{F} - \omega^2 \mathbf{G}^{-1} \right] \mathbf{A} = 0, \quad \text{or} \quad \left(\mathbf{G}^{1/2} \mathbf{F} \mathbf{G}^{1/2} - \omega^2 \right) \mathbf{A} = 0.
$$

$\rightarrow$ eigenvalues and eigenvectors within each irred.rep. independently.

Symmetry-projected density of modes

"Post-processing": first obtain eigenvector of each mode (no symmetry constraints), *then* project it according to irred.reps. *Advantage*: works also for solid solutions and otherwise "approximate symmetry".

$$I_\aleph^\nu(\omega) = \sum_i \left| \sum_{\alpha \in \aleph} \mathbf{A}_i^\alpha \, \mathbf{S}_i^{\alpha\nu} \right|^2 \delta(\omega - \omega_i) \, .$$

$\mathbf{S}_i^{\alpha\nu}$: projection vectors (in the 3-dim. space of individual atom displacements); ν: irreducible representation of underlyng (or, presumed, if "approximative") space group; i: mode index; α: atom index.

Where to get $\mathbf{S}_i^{\alpha\nu}$ (for example...) :
go to http://www.cryst.ehu.es (Bilbao crystallographic server),
specifically to its SAM section http://www.cryst.ehu.es/rep/sam.html ,
choose the space group, select a Wyckoff position, select "Show",
go to "Mechanical representation" and again select "Show".

An example: kesterite-type $Cu_2ZnSnSe_4$ (space group $I\bar{4}$)

Cu
Zn
Sn
Se
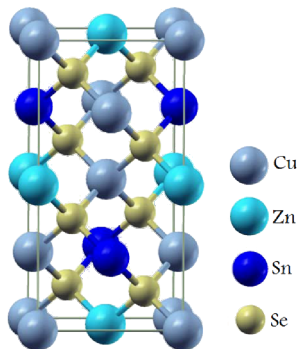
Symmetry coordinates in different vibration modes constructed from individual Cartesian displacements $\pm(X, Y, Z)$ of anions

| Modes	Anion sites: $(0\,0\,0)^+$; $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})^+$			
	$(\frac{1}{4}\,\frac{3}{4}\,\frac{1}{8})$	$(\frac{3}{4}\,\frac{1}{4}\,\frac{1}{8})$	$(\frac{3}{4}\,\frac{3}{4}\,\frac{7}{8})$	$(\frac{1}{4}\,\frac{1}{4}\,\frac{7}{8})$
A #1	Y	$-Y$	X	$-X$
A #2	$-X$	X	Y	$-Y$
A #3	$-Z$	$-Z$	Z	Z
B #1	Y	$-Y$	$-X$	X
B #2	$-X$	X	$-Y$	Y
B #3	Z	Z	Z	Z
(E^1+E^2) #1	X	X	——	——
(E^1+E^2) #2	Y	Y	——	——
(E^1+E^2) #3	Z	$-Z$	——	——
(E^1-E^2) #1	——	——	Y	Y
(E^1-E^2) #2	——	——	X	X
(E^1-E^2) #3	——	——	$-Z$	Z

Decomposition of vibration modes according to symmetries

Wyckoff positions	Irred. representations			(sums up to 8 at. ×3 = 24)
	A	B	E	
Cu (2a)		1	1	$1+1\times2 = 3$
Sn (2b)		1	1	$1+1\times2 = 3$
Cu (2c)		1	1	$1+1\times2 = 3$
Zn (2d)		1	1	$1+1\times2 = 3$
Se (8g)	3	3	3	$3+3+3\times2 = 12$

Symmetry coordinates (as above) for cations

| Modes	Wyckoff positions			
	(2a)	(2b)	(2c)	(2d)
B	Z	Z	Z	Z
(E^1+E^2)	X	X	X	X
(E^1-E^2)	Y	Y	Y	Y

CZTSe: Γ-vibrations and symmetry analysis
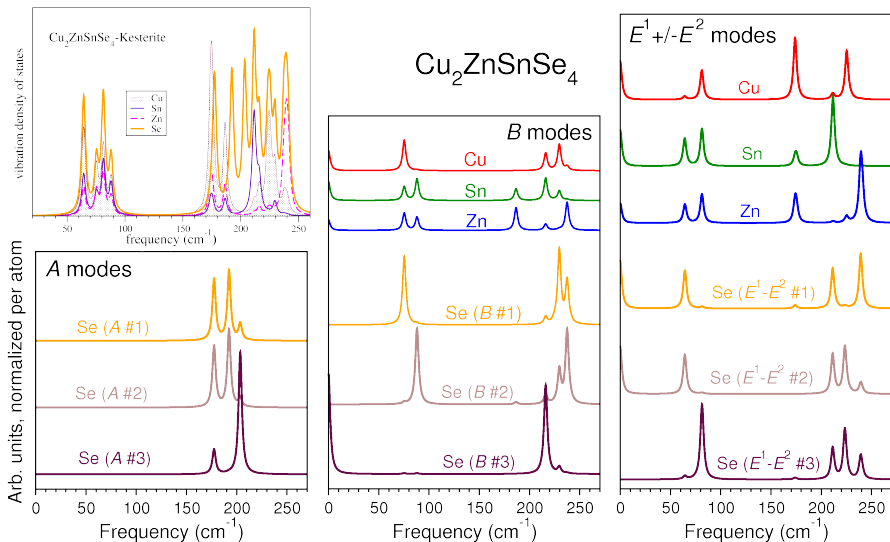
NB: within modes of the same symmetry block, and between partners of the same irreducible representation, the decomposition is ambiguous!

Cu_2SnSe_3 vs. $Cu_2ZnSnSe_4$: structure and phonons

$Cu_2ZnSnSe_4$ (CZTS) of kesterite-type structure (bct)
is a promising material for photovoltaics.
Cu_2SnSe_3 (CTSe) is one of "secondary phases" ($\rightarrow$ monoclinic)
frequent in the phase diagram of Cu–Sn–Se, useless for photovoltaics.

The two structures correspond to different cation arrangement on the same underlying (zincblende) lattice. They are indistinguishable in X-ray diffraction; our motivation was to pinpoint existing diferences in their vibration spectra (in view of identifying possible "vibrational fingerprints".
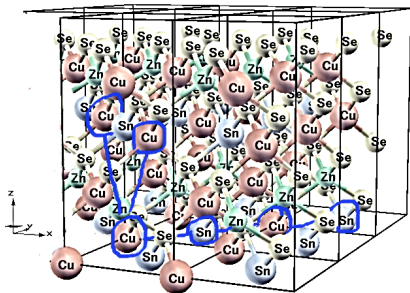
- monoclinic b axis along the [110] diagonal of the basal plane of kesterite;
- a, c vectors are valid lattice vectors of kesterite: $[\frac{1}{2} \ \frac{1}{2} \ \pm\frac{1}{2}]$;
- $3\times$ stapling of CZTSe kesterite (along monoclinic b) matches $2\times$ of CTSe
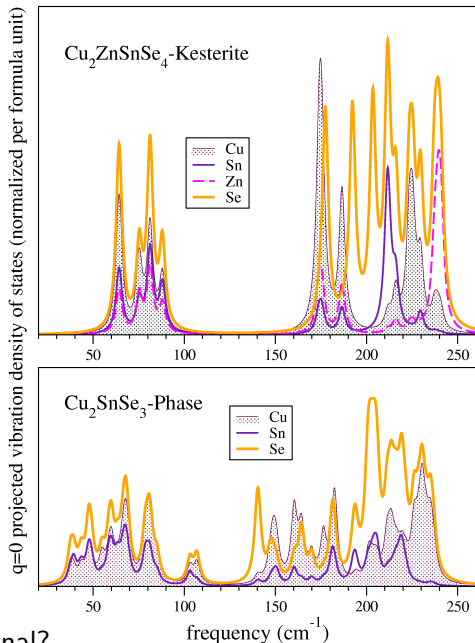
Density of modes at $\mathbf{q} = 0$

of supercell

N atoms $\rightarrow$ $3N$ modes ν, frequencies ω_ν, eigenvectors $A_\nu^{i\alpha}$
(i: cartesian x,y,z;
α: atom of species $\aleph$).

$$I_\aleph(\omega) = \sum_\nu \sum_{\alpha \in \aleph} \sum_i [A_\nu^{i\alpha}]^2 \, \delta(\omega - \omega_\nu)$$
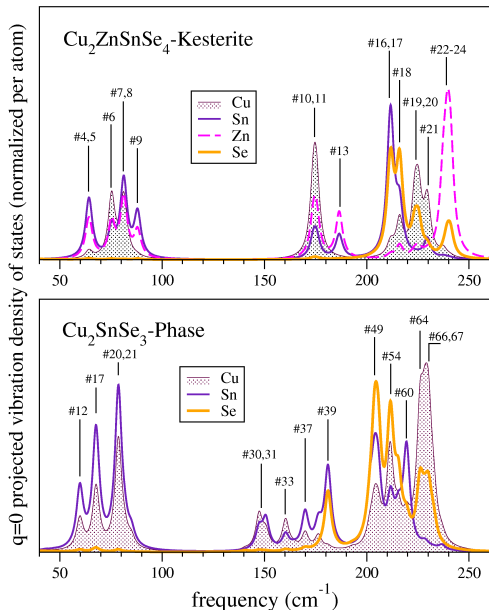
CZTSe: 8 at. / primitive cell,
CTSe: 24 at. / primitive cell

Formally, all are zone-center modes,
yet the spectrum is more rich
(as of a supercell...)

Do all these modes give a Raman signal?

Density of modes; **q**-projection

A "zincblende-like" **q**-projection

$$I_{\aleph}(\omega) = \sum_{\nu} \sum_{\substack{i \\ \alpha \in \aleph}} [A_{\nu}^{i\alpha} e^{i\mathbf{R}_{\alpha}\mathbf{q}}]^2 \, \delta(\omega - \omega_{\nu})$$

($\mathbf{q} = 0$ in the plot on the left):

Emphasizes "all cations against all anions" patterns (but not only, since projection for each species is done independently).

This recovers some similarity in spectra, and underlines the splitting of modes into three groups.

More in
J.Appl.Phys. **112**, 033719 (2012);
Phys.Rev.B **82**, 205204 (2010).

Vibration entropy (for phase diagrams calculations)

In a system of harmonic oscillators with mode density $g(\omega)$ obeying the Bose-Einstein statistics:
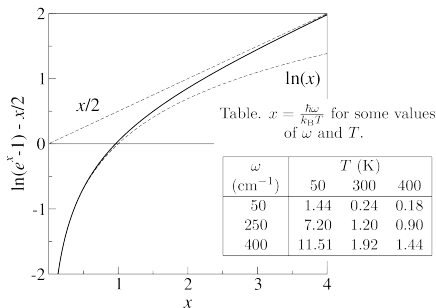
$$\text{free energy} \quad F \;=\; k_{\text{B}}T \int\limits_{0}^{\omega_{\text{max}}} \left[\ln(e^x - 1) - \frac{x}{2} \right] g(\omega)d\omega \quad \text{with} \; x = \frac{\hbar\omega}{k_{\text{B}}T} \,;$$

$$S = -\frac{\partial F}{\partial T} \;=\; k_{\text{B}} \int\limits_{0}^{\omega_{\text{max}}} \left[\frac{x}{e^x - 1} - \ln\big(1 - e^{-x}\big) \right] g(\omega)d\omega \,.$$

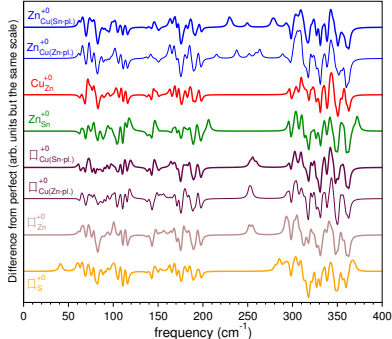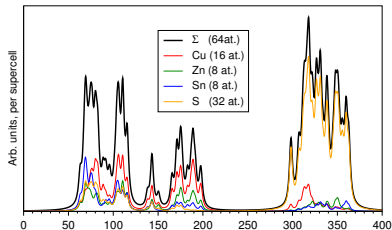In a large supercell, $\mathbf{q} = 0$ discrete spectrum samples the continuous density of modes:

$$g(\omega) \approx \sum_{\alpha} \delta(\omega - \omega_{\alpha}) \,.$$

The supercell may include defects with their (possibly) localized vibration modes.

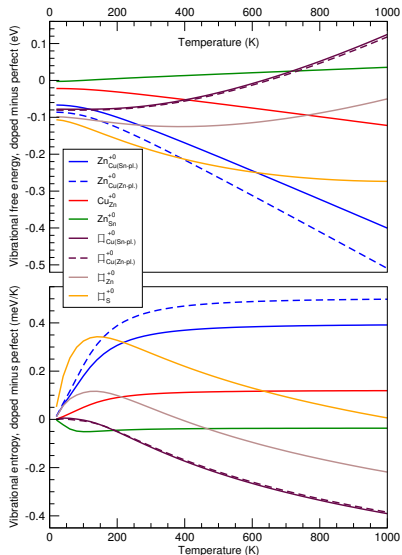Table. $x = \frac{\hbar\omega}{k_{\text{B}}T}$ for some values of ω and T.

ω	T (K)		
(cm^{-1})	50	300	400
50	1.44	0.24	0.18
250	7.20	1.20	0.90
400	11.51	1.92	1.44

Cu_2ZnSnS_4: 64-at. supercell, total density of modes

Vibrational properties of point defects in CZTS

Conclusion

- Calculated phonon eigenvectors contain very rich information which is often neglected, or used in cumulated form only. However, it can be conveniently extracted by applying a projection technique (with respect to properties of immediate interest).

- Projections to mention are onto atom / atom type (obvious), but also (less obvious) onto a $\mathbf{q}$-vector and onto a symmetry block (irreducible representation of the space group).

- Projection technique can also be applied to the study of *solid solutions*, when the nominal symmetry relations (with respect to translations / rotations) are not exactly valid. Still, the trends can be revealed (e.g., dispersion relations in an alloy, a routine issue of discussion in experimental works).

- The above projection tools are readily available for post-processing of SIESTA results [ask andrei.postnikov@univ-lorraine.fr]; for other codes, at most, some modification of data format may be needed.