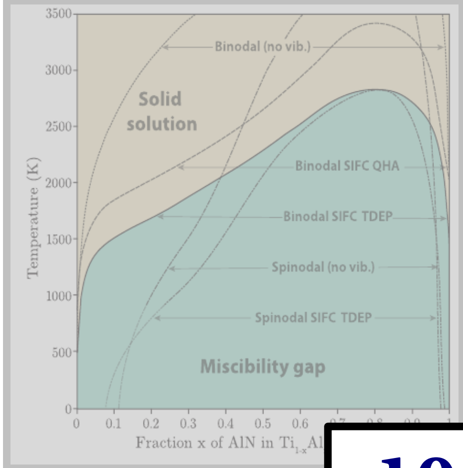
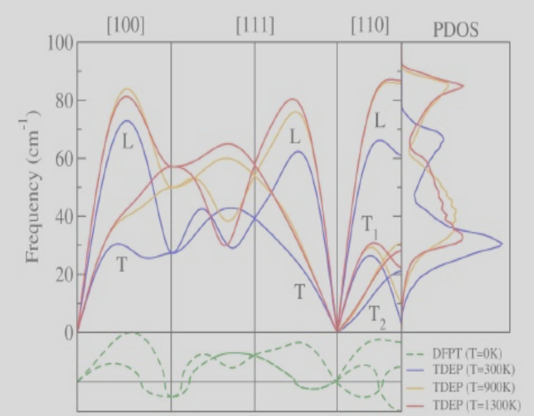
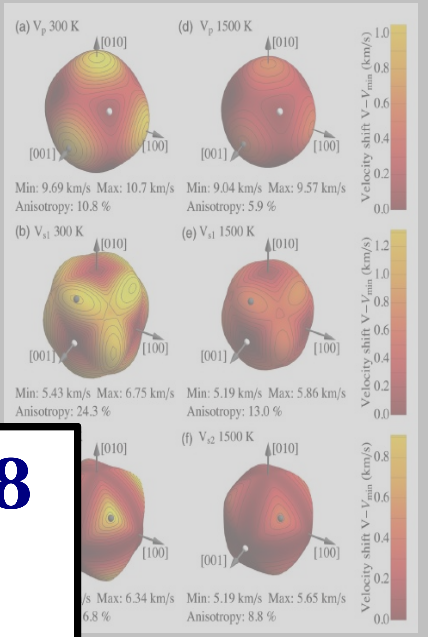
CECAM workshop

Anharmonicity and thermal properties of solids

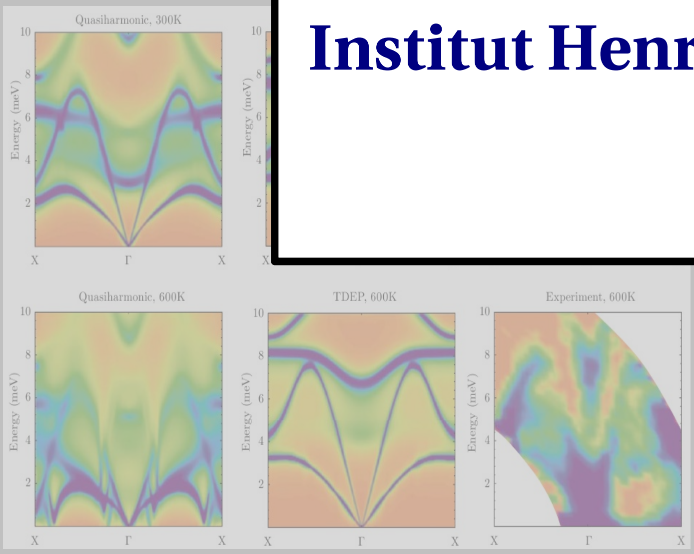


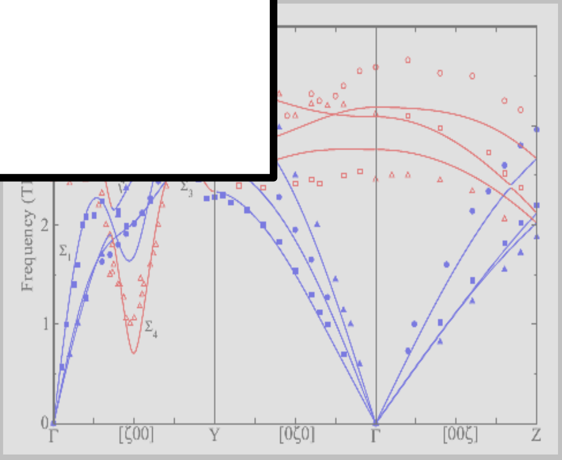




10-12 January 2018
Paris

Institut Henri Poincaré





Conference organizers

François Bottin (CEA-DIF, France)
Johann Bouchet (CEA-DIF, France)
Matthieu Verstraete (University of Liège, Belgium)
Olle Hellman (California Institute of Technology (Caltech), US)

Dear colleagues,

The quantitative prediction of harmonic phonon frequencies and thermodynamical quantities is one of the great successes of atomistic electronic structure in the past 30 years. Reality is however more complex, and vibrations are never purely harmonic. The systematic calculation of all possible anharmonic processes is a daunting task. Anharmonicity influences many important phenomena such as thermal expansion and Fourier's law or coherent phonon generation. Heat transport is a central pillar of solid state physics and engineering, and influences many devices and properties. Both low and high conductivity materials have their uses, but historically its control has proved elusive. Simple mechanistic (grind it up) or back of the envelope (make it heavy) models reached their limits years ago. But only in the past 10-15 years a full chemically specific and atomistic prediction of lattice thermal properties has become possible. The field has blossomed at the crossroads of Chemistry, Physics, Engineerings (Energy, Mechanical, Electronic etc...), and benefitted from a positive feedback loop through refined experiments and novel theories.

The aim of this workshop is to bring together cutting edge researchers in the numerical simulation and experimental determination of anharmonic phonon dynamics, and related properties (transport, ultrafast, electrons), to foster new approaches, new ideas, and give the field a decisive kick forward. We anticipate intense discussions and hotly contested debate about where to go from here, as the terrain is wide open.

It's a great pleasure to welcome you to Paris, and we look forward to a very fruitful workshop,

The organizers

Summary

The IHP (Institut Henri Poincaré)

The Henri Poincaré Institute (or IHP for Institut Henri Poincaré) is a mathematics research institute part of UPMC Sorbonne Universités, in association with the Centre national de la recherche scientifique (CNRS). It is located in the 5th arrondissement of Paris, on the Sainte-Geneviève Hill, close to a number of other higher education institutions.

Just after World War I, mathematicians Émile Borel in France and George Birkhoff in the United States persuaded American and French sponsors (Edmond de Rothschild and the Rockefeller Foundation respectively) to fund the building of a centre for lectures and international exchanges in mathematics and theoretical physics. The Institute was inaugurated on 17 November 1928 and named after French mathematician Henri Poincaré (1854-1912).

Right from the start, the institute's objective has been to promote mathematical physics, and it soon became a favourite meeting place for the French scientific community. In the 1990s, the IHP became a thematic institute modeled on Berkeley's Mathematical Sciences Research Institute (MSRI) and a place for contact making, exchange and diffusion of knowledge.

Many famous mathematicians and theoretical physicians have taught at this Institution since almost one century. We can cite the french scientists Henri Poincaré, Léon Brilouin, Henri Cartan, André Weil, Louis de Broglie, Émile Picard... but also numerous foreign scientists such as Paul Dirac, Albert Einstein, Enrico Fermi, Vito Volterra...

The IHP's governing board has about 25 members. There are no permanent researchers other than the director and the deputy director. Since 2009, the institute has been headed by mathematician Cédric Villani (director), Fields Medals laureate in 2010. The current deputy director is the French cosmologist Jean-Philippe Uzan.

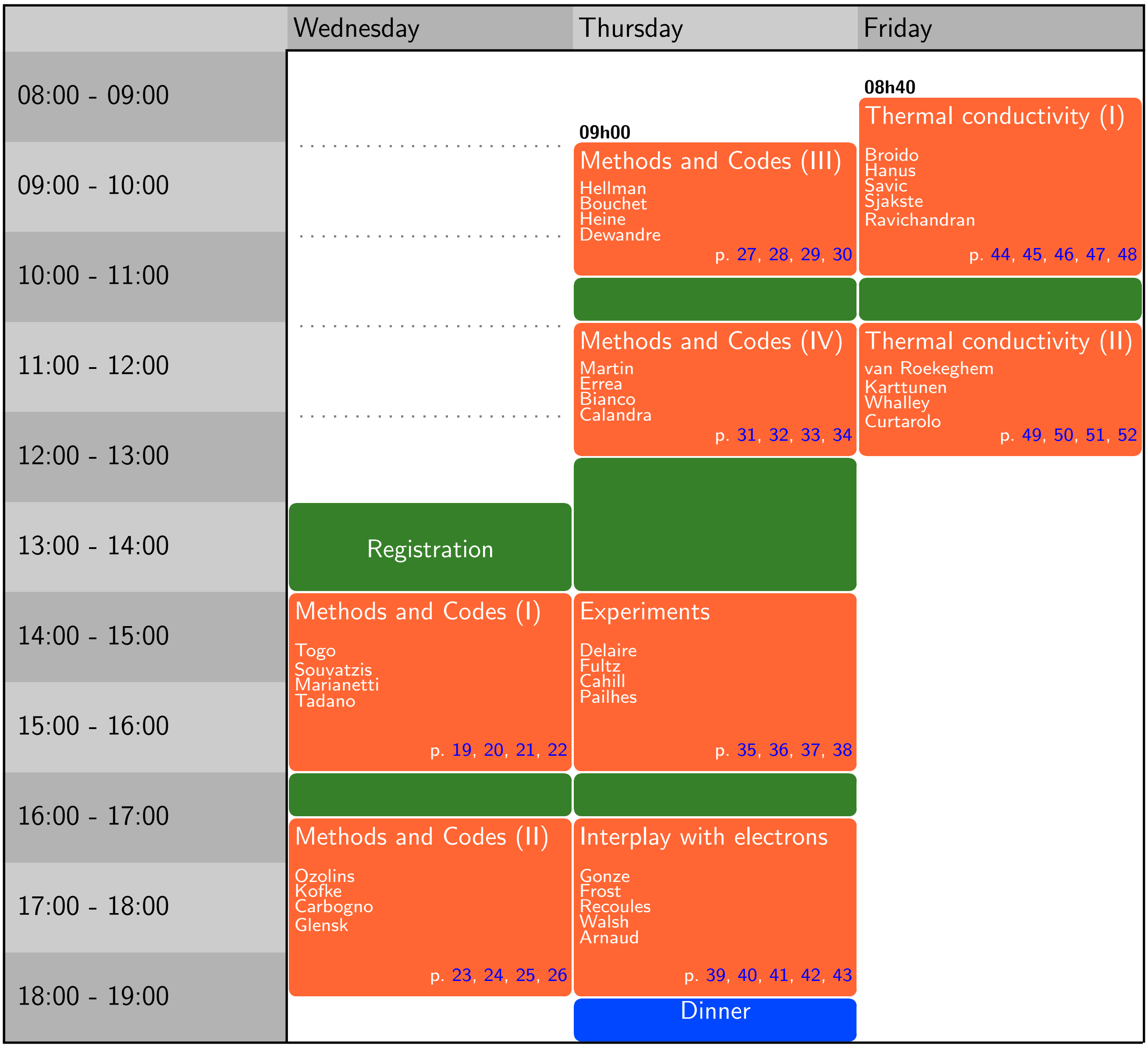
Bienvenue dans le Vème arrondissement de Paris

Participants

Name	Address	Country	email
Bernard Amadon	CEA Bruyeres	France	Bernard.Amadon@cea.fr
Brice Arnaud	University of Rennes	France	brice.arnaud@univ-lemans.fr
Unai Aseguinolaza	University of the Basque Country	Spain	uaseguinolaz001@ikasle.ehu.eus
Raffaelo Bianco	University of Sapienza	Italy	raffaello.bianco@roma1.infn.it
Jordan Bieder	CEA Bruyeres	France	jordan.bieder@cea.fr
Francois Bottin	CEA Bruyeres	France	francois.bottin@cea.fr
Johann Bouchet	CEA Bruyeres	France	johann.bouchet@cea.fr
David Broido	Boston College	US	david.broido@bc.edu
David Cahill	University of Illinois	US	d-cahill@uiuc.edu
Matteo Calandra	University of Pierre and Marie Curie	France	matteo.calandra@impmc.upmc.fr
Christian Carbogno	Max Planck (Berlin)	Germany	carbogno@fhi-berlin.mpg.de
Stefano Curtarolo	Duke University	US	stefano@duke.edu
Djordje Dangic	University College Cork	Ireland	djordje.dangic@tyndall.ie
Marc de Boissieu	University of Grenoble Alpes	France	Marc.de-boissieu@simap.grenoble-inp.fr
Olivier Delaire	Duke University	US	olivier.delaire@duke.edu
Agnes Dewaele	CEA Bruyeres	France	Agnes.Dewaele@cea.fr
Antoine Dewandre	University of Liege	Belgium	Antoine.Dewandre@ulg.ac.be
Boris Dorado	CEA Bruyeres	France	boris.dorado@cea.fr
Ion Errea	University of the Basque Country	Spain	ion.errea@ehu.eus
Brent Fultz	California Institute of Technology	US	btf@caltech.edu
Albert Glensk	Max-Planck-Institut, Düsseldorf	Germany	glensk@mpie.de
Xavier Gonze	University of Louvain	Belgium	xavier.gonze@uclouvain.be

Riley Hanus	Northwestern University	US	rhanus@u.northwestern.edu
Matt Heine	Boston College	US	heinema@bc.edu
Olle Hellmann	California Institute of Technology	US	olhel@ifm.liu.se
Gerald Jomard	CEA Cadarache	France	Gerald.Jomard@cea.fr
Antti Karttunen	University of Jyväskylä	Finland	antti.j.karttunen@iki.fi
David Kofke	University of Buffalo	US	kofke@buffalo.edu
Chris Marianetti	Columbia University	US	chris.marianetti@columbia.edu
Alexandre Martin	University of Liege	Belgium	Alexandre.martin@ulg.ac.be
Jarvist Moore Frost	Imperial College of London	UK	jarvist.frost@ic.ac.uk
Vidvuds Ozolins	University of California	US	vidvuds.ozolins@yale.edu
Stéphane Pailhès	Institute Light and Matter (ILM), Lyon	France	stephane.pailhes@univ-lyon1.fr
Navaneeth Ravichandran	Boston College	US	navaneeth.ravichandran@bc.edu
Vanina Recoules	CEA Bruyeres	France	Vanina.recoules@cea.fr
Guido Roma	CEA Saclay	France	roma@cea.fr
Ivana Savic	Tyndall National Institute, Cork	Ireland	ivana.savic@tyndall.ie
Jelena Sjakste	Ecole Polytechnique	France	jelena.sjakste@polytechnique.edu
Francois Soubiran	ENS Lyon	France	francois.soubiran@ens-lyon.org
Petros Souvatzis	Uppsala University	Sweden	petros.souvatzis@gmail.com
Terumasa Tadado	University of Tokyo	Japan	terumasa.tadano@gmail.com
Atsushi Togo	Kyoto University	Japan	togo.atsushi.f40@kyoto-u.jp
Marc Torrent	CEA Bruyeres	France	Marc.Torrent@cea.fr
Florian Trybel	University of Bayreuth	Germany	f.trybel@uni-bayreuth.de
Ambroise Van Roekeghem	LITEN (CEA, Grenoble)	France	ambroise.vanroekeghem@cea.fr
Matthieu Verstraete	University of Liege	Belgium	Matthieu.Verstraete@ulg.ac.be
Aron Walsh	Imperial College of London	UK	a.walsh@imperial.ac.uk
Lucy Whalley	Imperial College of London	UK	lw3016@ic.ac.uk

Program



	Wednesday	Thursday	Friday
08:00 - 09:00			**08h40** Thermal conductivity (I) Broido Hanus Savic Sjakste Ravichandran p. 44, 45, 46, 47, 48
09:00 - 10:00		**09h00** Methods and Codes (III) Hellman Bouchet Heine Dewandre p. 27, 28, 29, 30	
10:00 - 11:00			
11:00 - 12:00		Methods and Codes (IV) Martin Errea Bianco Calandra p. 31, 32, 33, 34	Thermal conductivity (II) van Roekeghem Karttunen Whalley Curtarolo p. 49, 50, 51, 52
12:00 - 13:00			
13:00 - 14:00	Registration		
14:00 - 15:00	Methods and Codes (I) Togo Souvatzis Marianetti Tadano p. 19, 20, 21, 22	Experiments Delaire Fultz Cahill Pailhes p. 35, 36, 37, 38	
15:00 - 16:00			
16:00 - 17:00	Methods and Codes (II) Ozolins Kofke Carbogno Glensk p. 23, 24, 25, 26	Interplay with electrons Gonze Frost Recoules Walsh Arnaud p. 39, 40, 41, 42, 43	
17:00 - 18:00			
18:00 - 19:00		Dinner	

Wednesday - 10.01.2018

13.00-14.00	Registration		
1st Session : Methods and Codes (I)			
14.00-14.30	Atsushi Togo	Software development of phonon calculation code and some activities related to phonon anharmonicity	p.19
14.30-15.00	Petros Souvatzis	Assuming ergodicity and calculating phonon life-times by the SCAILD method and how to treat problems with optical modes within the SCAILD method.	p.20
15.00-15.30	Chris Marianetti	An optimal approach to computing phonons and their interactions via finite difference	p.21
15.30-16.00	Terumasa Tadano	Understanding the Role of Quartic Anharmonicity in Solids using First-Principles Lattice Dynamics	p.22
16.00-16.30	Coffee Break		
2nd Session : Methods and Codes (II)			
16.30-17.00	Vidvuds Ozolins	A first-principles approach to anharmonic effects in alloys	p.23
17.00-17.30	David Kofke	Harmonically Mapped Averaging for Direct Evaluation of Anharmonic Properties of Solids by Molecular Simulation	p.24
17.30-18.00	Christian Carbogno	Strongly Anharmonic Nuclear Dynamics in Solids: Accurate Computations and Rapid Estimates	p.25
18.00-18.30	Albert Glensk	From thermodynamics to phonon lifetimes: Anharmonic calculations with ab inito accuracy	p.26

Thursday - 11.01.2018

3rd Session : Methods and Codes (III)			
09.00-09.30	Olle Hellman	Non-harmonic modelling of materials	p.27
09.30-09.50	Johann Bouchet	Phase transition at high pressure and high temperature in MgO	p.28
09.50-10.10	Matthew Heine	Temperature dependent magnetic effects on phonon modes	p.29
10.10-10.30	Antoine Dewandre	Finite temperature vibrational and thermal properties of Dichalcogenides	p.30
10.30-11.00	Coffee Break		
4th Session : Methods and Codes (IV)			
11.00-11.20	Alexandre Martin	The MULTIBINIT software project	p.31
11.20-11.50	Ion Errea	Anharmonic Properties of Solids within the Stochastic Self-Consistent Harmonic Approximation: Phonons, Second-Order Structural Phase Transitions, and Thermal Properties	p.32
11.50-12.10	Matteo Calandra	Anharmonic phonon spectra of Mono and Dichalcogenides in the self-consistent harmonic approximation	p.34
12.10-12.30	Raffaello Bianco	Anharmonic phonons and second-order phase-transitions by the stochastic self-consistent harmonic approximation	p.33
12.30-14.00	Lunch		
5th Session : Experiments			

14.00-14.30	Olivier Delaire	Phonon Anharmonicity near Lattice Instabilities: First-Principles Simulations and Scattering Experiments	p.35
14.30-15.00	Brent Fultz	New directions for inelastic neutron scattering studies of anharmonic phonons	p.36
15.00-15.30	David Cahill	Testing models of heat transport using high hydrostatic pressure and anharmonicty of lattice vibrations	p.37
15.30-16.00	Stephane Pailhes	Investigation of phonon states in a poor thermal crystalline conductor by means of inelastic scattering spectroscopy	p.38
16.00-16.30	Coffee Break		
6th Session : Interplay with electrons			
16.30-17.00	Xavier Gonze	Temperature dependence of the electronic structure : the direct and indirect roles of phonons	p.39
17.00-17.20	Jarvist Moore Frost	Device physics repercussion of semiconductor anharmonicity: halide perovskites	p.40
17.20-17.40	Vanina Recoules	Phonons properties of two temperature metals	p.41
17.40-18.00	Aron Walsh	Extreme anharmonicity in metal-organic frameworks: challenges and opportunities	p.42
18.00-18.20	Brice Arnaud	Coherent phonon dynamics in bismuth: A quantitative study of phonon-phonon and electron-phonon coupling	p.43

Friday - 12.01.2018

7th Session : Thermal Conductivity (I)			
08.40-09.10	David Broido	Achieving high thermal conductivity from weak anharmonic phonon scattering	p.44
09.10-09.30	Riley Hanus	Phonon diffraction and dimensionality crossover in phonon-interface scattering	p.45
09.30-09.50	Ivana Savic	Thermal properties of PbTe and GeTe based materials near ferroelectric phase transition	p.46
09.50-10.10	Jelena Sjakste	Thermal properties of bismuth and bismuth nanostructures calculated ab initio.	p.47
10.10-10.30	Navaneeth Ravichandran	Ab-initio thermal properties of semiconductors with higher order anharmonicities	p.48
10.30-11.00	Coffee Break		
8th Session : Thermal Conductivity (II)			
11.00-11.30	Ambroise van-Roekeghem	High-throughput finite-temperature properties of oxide and fluoride perovskites	p.49
11.30-11.50	Antti Karttunen	Predicting the lattice thermal conductivity of transition metal oxides and inorganic-organic superlattices with dispersion-corrected hybrid density functional methods	p.50
11.50-12.10	Lucy Whalley	Breaking periodicity: vibrations of defects in photovoltaic materials	p.51
12.10-12.30	Stefano Curtarolo	Novel high-entropy carbides discovered by synthesizability descriptors	p.52

Oral Presentations

Contents

O.1 Software development of phonon calculation code and some activities related to phonon anharmonicity

Atsushi Togo[1], Isao Tanaka[1,2]

[1] *Elements Strategy Initiative for Structural Materials, Kyoto university*
[2] *Department of Materials Science and Engineering, Kyoto university*

The software phonopy[1] is a phonon calculation code, which employs the supercell approach and relies on the first-principles calculation codes as force calculators. The source code is licensed under BSD-3 and the repository is available on GitHub[2]. Phonopy is used by many users. To support thousands of users, the software is expected to be robust and user friendly. Bug fix, answering users' questions and implementing requested features are important pieces of the software development. Documentation is as important as the code itself for users. The Python Sphinx software is used to write the phonopy document to easily describe mathematical formulae.

Phonopy is written in Python. By using Python, the code becomes more readable and the time needed for the computer implementation is saved. The computationally heavy routines are written in C and are called as Python modules via the Python/C API. When implementing a new feature, initially it is written in Python as a prototype. Once it is found too heavy for Python, the code is ported to C, which is easy. For normal use cases, harmonic phonon calculation is an easy Python and C, the overhead to copy data is negligible by using C task for the recent computers. Therefore multithreading computation is unsupported. By this, possible installation failure by users can be avoided. PyPi and conda package installations are supported. Its test and deployment system on Travis CI is developed by Paweł T. Jochym. By him, Linux, Windows, and macOS binary packages are prepared at the conda-forge channel. To support Windows, the C code has to be written in C89 at this moment. Phonopy can be called as a Python module via its API. This may be useful for some users since phonon calculations are executed programmatically. Using the phonopy API, we automated computations of phonons of ten thousand compounds and made a phonon calculation database[3].

Apart from phonopy, we have developed a phonon-phonon interaction calculation code, phono3py[4]. This can handle only three phonon processes within perturbation regime. This code is also written in Python. The OpenMP multithreaded code is written in the C side to finish the calculations in a reasonable time frame. This code requires to treat large data. Memory space needed for the data is allocated mainly by Numpy on the Python side. Since the data are passed to the C side as a C pointer, copy of the data is avoided, which is the important issue to save both memory space and computational time. A direct solution of linearized phonon Boltzmann equation[5] is implemented. Diagonalization of a big collision matrix is required by this method and is achieved using LAPACK. It is convenient for users to use Intel MKL multithreaded BLAS through the Numpy conda distribution to finish the calculation in a reasonable time frame. A code to extract quasi-particle phonons from molecular dynamics simulation by projecting atomic velocities on harmonic phonon eigenvectors, dynaphopy[6], is developed by Abel Carreras and us.

We are interested in measuring phonon linewidths of crystals by inelastic X-ray scattering at Spring8 in Japan. We may show our preliminary results briefly.

[1] See the URL: https://atztogo.github.io/phonopy/
[2] See the URL: https://github.com/atztogo/phonopy/
[3] See the URL: http://phonondb.mtl.kyoto-u.ac.jp/
[4] See the URL: https://atztogo.github.io/phono3py/
[5] L. Chaput, Phys. Rev. Lett. **110** (2013) 265506.
[6] See the URL: http://abelcarreras.github.io/DynaPhoPy/

O.2 Assuming ergodicity and calculating phonon life-times by the SCAILD method and how to treat problems with optical modes within the SCAILD method.

Petros Souvatzis[1]

[1] *Banérgatan 12 A, 75 237 Uppsala, Sweden.*

Phonon lifetime calculations from first principles usually rely on time-consuming molecular dynamics calculations, or density functional perturbation theory where the zero-temperature crystal structure is assumed to be dynamically stable. By assuming that the phase space sampling of the self-consistent ab initio lattice dynamical method[1](SCAILD) method is ergodic, a new and effective method for calculating phonon lifetimes from first principles can be realized. This method is not limited to crystallographic phases stable at 0 K and provides a scheme more effective than most corresponding molecular dynamics calculations. The method is here tested by calculating the bcc phase phonon lifetimes of Li, Na, Ti and Zr as representative examples.[2]

Furthermore, some thoughts are here presented on how to deal with the problems with utilizing the SCAILD method when the number of optical modes is large.

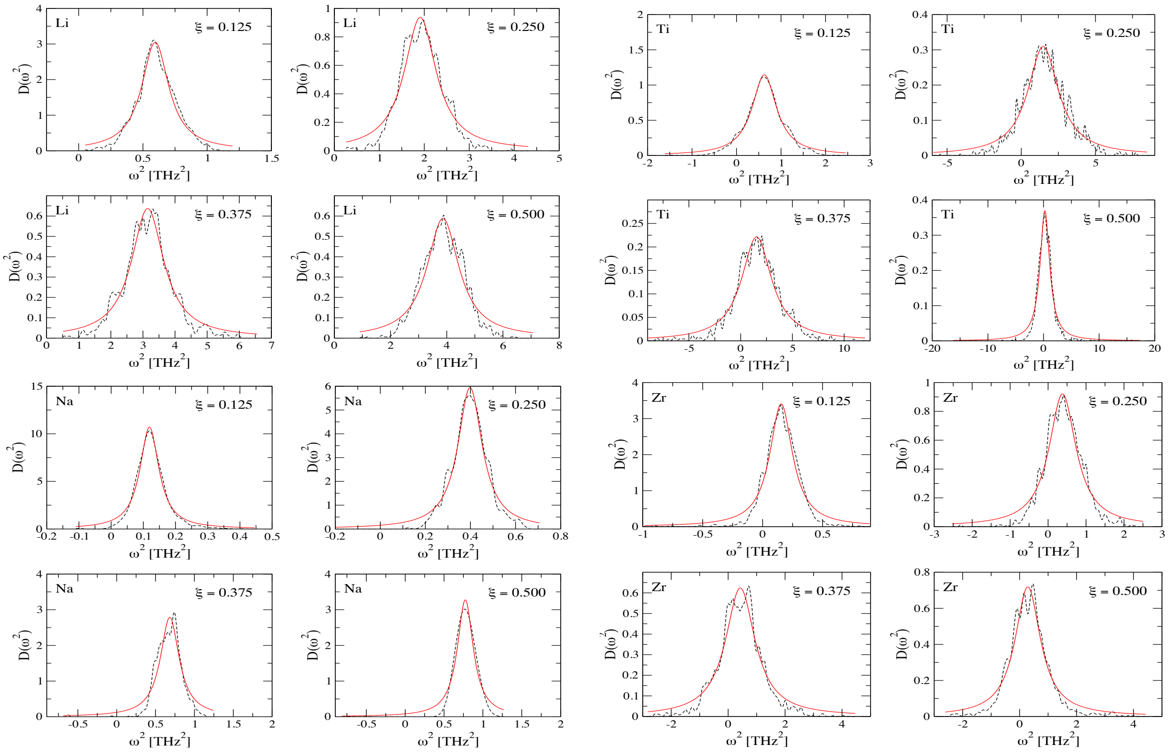


Figure O.1: Calculated phonon spectra for Li, Na, Ti and Zr at different wave-vectors.

[1] P. Souvatzis *et al*, Phys. Rev. Lett **100**, 095901 (2008)
[2] P. Souvatzis, J. Phys.: Condens. Matter **23** (2011) 445401

O.3 An optimal approach to computing phonons and their interactions via finite difference

Chris Marianetti[1]

[1] *Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York 10027, USA*

Efficiently extracting a high resolution Taylor series expansion of the Born-Oppenheimer surface from an arbitrary first-principles approach is of great importance. Here we present an optimal formalism to compute phonons and their interactions at arbitrary order on a uniform grid using finite difference. Our approach ensures that a given derivative is always obtained from the smallest possible supercell dictated by the translation group, in addition to the smallest number of runs dictated by space group symmetry. We demonstrate that our approach is superior to any single-supercell finite difference approach, which is commonplace in the literature for phonons and cubic interactions. Applications are presented for graphene, providing phonons and interactions up to 5th order at an unprecedented q-space resolution with minimal discretization errors.

O.4 Understanding the Role of Quartic Anharmonicity in Solids using First-Principles Lattice Dynamics

Terumasa Tadano[1], Shinji Tsuneyuki[2]

[1] *National Institute for Materials Science (NIMS), Tsukuba, Japan*
[2] *University of Tokyo, Tokyo, Japan*

The anharmonicity of lattice vibration characterizes various thermal properties of solids including the coefficient of thermal expansion (CTE), lattice thermal conductivity (LTC), and the temperature dependence of phonon frequencies. Owing to the recent developments of first-principles methods to compute second- and third-order interatomic force constants, it is now rather straightforward to predict CTE and LTC of various materials based, respectively, on the quasiharmonic theory and the perturbation theory. However, the effects of quartic and higher-order anharmonicity neglected in the conventional methods can be significant in many solids. Indeed, they are essential in many thermoelectric materials including SnSe and clathrates.

To elucidate the role of quartic anharmonicity in solids, we have developed a first-principles method to compute temperature-dependent phonon properties [1,2]. The method is based on the self-consistent phonon (SCP) theory, and the frequency renormalization due to the quartic anharmonicity is calculated at the mean-field level. We have applied the method to $SrTiO_3$ [1,2], SnSe, and clathrates [3,4] and shown that the phonon frequency renormalization dramatically affects the calculated LTC values. We have also applied the SCP method to understand the atomistic origin of the negative thermal expansion of ScF_3 [5].

In this talk, we present the theoretical and technical details of our SCP approach and show its validity for studying thermal properties of strongly anharmonic solids. If we have some time left, we also introduce the recent developments of the open source software ALAMODE [6].

[1] T. Tadano and S. Tsuneyuki, Phys. Rev. B **92** (2015) 054301.
[2] T. Tadano and S. Tsuneyuki, arXiv:1706.04744 (J. Phys. Soc. Jpn. in press).
[3] T. Tadano, Y. Gohda, and S. Tsuneyuki, Phys. Rev. Lett. **114** (2015) 095501.
[4] T. Tadano and S. Tsuneyuki, arXiv:1710.00311.
[5] Y. Oba, T. Tadano, R. Akashi, and S. Tsuneyuki, in preparation.
[6] ALAMODE: `http://ttadano.github.io/alamode/`

O.5 A first-principles approach to anharmonic effects in alloys

Vidvuds Ozolins[1,2]

[1] *Department of Applied Physics, Yale University, New Haven, CT, 06520, USA*
[2] *Yale Energy Sciences Institute, West Haven, CT, 06516, USA*

Alloying is a widely used technique for changing lattice dynamical properties and thermodynamic phase stability of crystalline solids such as ferroelectrics, thermoelectrics, metallic alloys, and shape memory materials. The need to include phonon scattering due to mass and force constant disorder on equal basis with anharmonic phonon-phonon interactions are serious challenges for accurate theoretical modeling. First-principles approaches based on the density-functional theory (DFT) have been particularly difficult to develop due to the high computational cost of direct simulations and technical difficulties involved in parameterizing interatomic interactions. We present a systematic approach to constructing lattice dynamics Hamiltonians for dilute and concentrated alloys based on compressive sensing. Our approach allows to extend the reach of DFT to nanosecond time scales, enabling direct simulation of thermodynamic and thermal transport properties of alloys. Examples from the field of thermoelectric materials (Si-Ge and PbTe-PbSe) will be presented to illustrate the advantages of our approach.

O.6 Harmonically Mapped Averaging for Direct Evaluation of Anharmonic Properties of Solids by Molecular Simulation

Andrew J. Schultz[1], Sabry G. Moustafa[1], David A. Kofke[1]

[1] *Department of Chemical & Biological Engineering, University at Buffalo, Buffalo, NY 14260-4200, USA*

”Mapped averaging” is a recently published framework for the reformulation of ensemble averages [1]. The treatment uses approximate results from statistical mechanical theory to derive new ensemble averages (mapped averages) that represent exactly the error in the theory. Well-conceived mapped averages can be computed by molecular simulation with remarkable precision and efficiency; in favorable cases the computational savings are many orders of magnitude. For crystalline systems, a harmonic approximation provides a suitable starting point, yielding expressions that separate the known harmonic behavior from residual averages, which thus encapsulate anharmonic contributions to the properties [2]. With harmonic contributions removed, direct measurement of these anharmonic contributions by molecular simulation can be accomplished without contamination by noise produced by the already-known harmonic behavior. We demonstrate this harmonically mapped averaging (HMA) scheme with applications to the Lennard-Jones model and to metallic systems modeled with electronic density functional theory. We find that first-derivative properties (pressure, energy) can be obtained to a given precision via HMA at least 10 times faster than by using conventional averaging, and second-derivative properties (e.g., heat capacity) are obtained at least 100 times faster; in more favorable cases, the speedup exceeds a millionfold. Free-energy calculations are accelerated by 50 to 1000 times [3]. Data obtained using HMA formulations are rigorous and not subject to any added approximation, and in fact are less sensitive to inaccuracies relating to finite-size effects, potential truncation, equilibration, and similar considerations. Moreover, the approach does not require any alteration in how sampling is performed during the simulation, so it may be used with standard Monte Carlo or molecular dynamics methods. However, the mapped averages do require evaluation of first and second derivatives of the intermolecular potential, for evaluation of first and second thermodynamic-derivative properties, respectively. Apart from its usefulness to simulation, the HMA formalism may constitute a basis for new theoretical treatments of crystals.

[1] A. J. Schultz, S. G. Moustafa, W. Lin, S. J. Weinstein, and D. A. Kofke, ”Reformulation of Ensemble Averages via Coordinate Mapping”, J. Chem. Theory Comput. **12**, 1491 (2016)
[2] S. G. Moustafa, A. J. Schultz, and D. A. Kofke, ”Very fast averaging of thermal properties of crystals by molecular simulation”, Phys. Rev. E **92**, 043303 (2015).
[3] S. G. Moustafa, A. J. Schultz, and D. A. Kofke, ”Harmonically Assisted Methods for Computing the Free Energy of Classical Crystals by Molecular Simulation: A Comparative Study”, J. Chem. Theory Comput. **13**, 825 (2017).

O.7 Strongly Anharmonic Nuclear Dynamics in Solids: Accurate Computations and Rapid Estimates

Christian Carbogno and Matthias Scheffler

Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, 14195 Berlin, Germany.

Many important material properties such as the thermodynamic stability and the lattice heat conductivity are influenced or even completely governed by the anharmonicity of the potential-energy surface (PES), i.e., by features of the PES that are not captured by a harmonic second-order Taylor expansion. Typically, such vibrational effects are only treated perturbatively in first-principles calculations by solely accounting for the leading contribution to anharmonicity, i.e., the third-order term in a Taylor expansion of the PES.[1,2] Despite the fact that such an approximated PES is known to be unphysical,[3] very little is yet known about the role of higher-order terms, which require a full *ab initio* molecular dynamics (AIMD) treatment.

In this work, we present a recently introduced formalism that allows to account for **all** anharmonic effects in the computation of thermal conductivities.[4] We discuss the underlying unique first-principles definition of the heat flux that allows to evaluate thermal conductivities via the Green-Kubo formulism from equilibrium AIMD trajectories. Incoherent and strongly anharmonic effects are directly treated within the real-space AIMD, while coherent, (almost) harmonic processes are mapped into a reciprocal-space representation, where they can be evaluated more efficiently. This robust, asymptotically exact scheme allows extrapolating such AIMD calculations on finite time and length scales to the macroscopic limit of bulk materials. We carefully validate and discuss the involved conceptual and numerical approaches for various representative examples with increasing degree of anharmonicity (e.g. Si, Ga_2O_3, CsCl, ZrO_2) by comparing the obtained AIMD results to perturbative calculations.[2] These investigations reveal that a correct treatment of higher-order anharmonicity plays a minor role in good thermal conductors, but is essential to achieve quantitative predictions and qualitative insights in highly anharmonic systems. In turn, we show how these insights can be exploited to design materials in which heat transport is promoted or hindered.[5] Eventually, we critically discuss the computational cost of such AIMD calculations and strategies to reduce it, e.g., with temperature-dependent Taylor expansions of the PES.[6,7]

[1] D. A. Broido, *et al.*, Appl. Phys. Lett. **91**, 231922 (2007).
[2] A. Togo, L. Chaput, and I. Tanaka, Phys. Rev. B **91**, 094306 (2015).
[3] G. Baym, Phys Rev **117**, 886 (1960).
[4] C. Carbogno, R. Ramprasad, and M. Scheffler, Phys. Rev. Lett. **118**, 175901 (2017).
[5] C. Carbogno *et. al.*, Phys. Rev. B **90**, 144109 (2014).
[6] K. Esfarjani and H. T. Stokes, Phys. Rev. B **77**, 144112 (2008).
[7] O. Hellman, *et. al.*, Phys. Rev. B **87**, 104111 (2013).

O.8 From thermodynamics to phonon lifetimes: Anharmonic calculations with ab intio accuracy

Albert Glensk[1], Dominique Korbmacher[1], Blazej Grabowski[1], Tilmann Hickel[1], Joerg Neugebauer[1]

[1] *Max-Planck-Institut für Eisenforschung GmbH, D-40237, Düsseldorf, Germany*

The calculation of thermodynamic materials properties with meV precision, has been a major challenge for the last decades. We have recently developed numerically exact ab initio approaches that provide the anharmonic contribution to free energies at all relevant temperatures. The application of these methods to stable systems[1], the dynamically unstable bcc Ti[2] and defects in Ni, Cu and Al[3,4] will be presented in the first part of the talk and compared with alternative approaches.

In the second part we will discuss the extension to spectrally resolved quantities such as frequencies and especially phonon lifetimes. Aiming again at the full temperature dependence up to melting, we go beyond density functional perturbation theory (DFPT) and perform the above mentioned fully ab initio MD simulations [1,5,6]. In this way we are able to identify the impact of approximations on phonon lifetimes and can outline promising strategies for an efficient determination of highly accurate materials properties.

[1] A. Glensk, B. Grabowski, T. Hickel, and J. Neugebauer, Phys. Rev. Lett. **114**, 1 (2015).
[2] D. Korbmacher, A. Glensk, B. Grabowski, J. Neugebauer, A. Duff, M. Finnis (in prepartion).
[3] Y. Gong, R.C. Reed, B. Grabowski, A. Glensk and J. Neugebauer (to be submitted).
[4] A. Glensk, B. Grabowski, T. Hickel, and J. Neugebauer, Phys. Rev. X **4**, 11018 (2014).
[5] A. Glensk, B. Grabowski, T. Hickel, J. Neugebauer, M. Leitner, J. Neuhaus and W. Petry (in preparation).
[6] A. Duff, T. Davey, D. Korbmacher, A. Glensk, B. Grabowski, J. Neugebauer and M. Finnis, Phys. Rev. B **91**, 214311 (2015).

O.9 Non-harmonic modelling of materials

Olle Hellman

Division of Engineering and Applied Science, California Institute of Technology, Pasadena, California 91125, USA

I will present methodological developments and applications of finite temperature simulations using ab initio molecular dynamics to generate an effective Hamiltonian that reproduce experimental neutron scattering spectra, thermal conductivity, phonon self energies, and heat capacities. I will present some idea around benchmarking and treatment of numerical noise, as well as future directions.

O.10 Phase transition at high pressure and high temperature in MgO

Johann Bouchet[1], François Bottin[1], Vanina Recoules[1]

[1] *CEA de Bruyères-le-Châtel, 91297 Arpajon Cedex, France.*

Usually, thermal vibrations of atoms can be taken into account via the so-called quasiharmonic approximation (QHA). In this framework, the phonon dispersion relations are calculated at 0 K using density functional perturbation theory (DFPT) and the temperature is included only via the thermal dilatation, i.e., by computing the phonon spectrum at different volumes. The main drawback of this approximation is that its accuracy is difficult to assess since anharmonic contributions beyond quasiharmonicity are difficult to estimate. But even if the harmonic part of the atomic vibrations dominate the free energy at elevated temperatures, the anharmonic contribution can play a crucial role to predict the transition pressure. For example in MgO, ab-initio calculations predict the transition phase B1-B2 at 0 K with a good agreement (6%) and the discreprancies can be accounted for by the choice of the functional (LDA or GGA) [1,2,3,4]. At high temperature, the discrepancies reach 30 %, and can only be explained by the treatment of the anharmonic contribution, see figure O.2. Here we will present a recent method, called the temperature dependent energy potential (TDEP)[5,6] that provides a consistent way to extract the best possible harmonic (or higher order) potential energy surface at finite temperatures. We will present our results for the B1-B2 phase transition and we will compare the TDEP method with previous calculations and recent experiments.

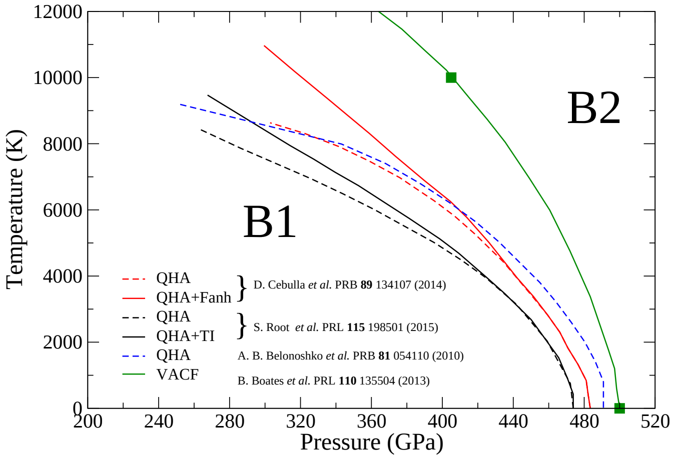


Figure O.2: Theoretical B1-B2 phase boundary of MgO.

[1] A. Belonoshko, S. Arapan, R. Martonak and A. Rosengren, Phys. Rev. B **81**, 054110 (2010).
[2] D. Cebulla and R. Redmer, Phys. Rev. B **89**, 134107 (2014).
[3] B. Boates and S. A. Bonev, Phys. Rev. Lett **110**, 135504 (2013).
[4] S. Root, L. Shulenburger, R. W. Lemke, D. H. Dolan, T. R. Mattsson and M. P. Desjarlais, Phys. Rev. Lett **115**, 198501 (2015).
[5] O. Hellman, I. A. Abrikosov and S. I. Simak, Phys. Rev. B **84**, 180301 (2011).
[6] J. Bouchet and F. Bottin, Phys. Rev. B **95** (5), 054113 (2017)

O.11 Temperature dependent magnetic effects on phonon modes

Matthew Heine[1], Olle Hellman[1,2,3] et David Broido[1]

[1] *Boston College, Chestnut Hill, MA, USA*
[2] *Linköping University, Linköping, Sweden*
[3] *California Institute of Technology, Pasadena, CA, USA*

Magnetic materials are important to a wide array of applications from steel to computer memory technology. Understanding the thermodynamics of these materials in such applications is often crucial. We present a methodology to calculate, from first principles, the effects of temperature and magnetism on the lattice dynamics.

Inclusion of magnetism involves a departure from the harmonic approximation of the lattice. Consider a simple Heisenberg model material; the strengths of the magnetic exchange parameters depend on the positions of the ions and so the magnetic portion of the Hamiltonian is coupled to the lattice dynamics. Magnetism can therefore, for instance, renormalize the phonon modes. This effect can be quite dramatic, even bringing about the stability of the lattice structure, just as thermal effects alone can bring about structural stability in non-magnetic materials.

Because the magnitude of the magnetic interaction between ions depends on the relative orientation of the spins as well as the positions of the ions, an accurate treatment requires inclusion of thermal effects, which introduce disorder in the spin configurations as well as the ion positions. Therefore we capture this behavior with first principles calculations via the Temperature Dependent Effective Potential (TDEP)[1,2] approach, performing noncolinear constrained magnetic moment calculations in the framework of Density Functional Theory (DFT)[3,4]

As an example, we calculate renormalized phonon modes in bulk BCC Fe, demonstrating excellent agreement with measured data as well as showing that the magnetism actually brings about the dynamic stability of the BCC structure in Fe.

[1] O. Hellman, P. Steneteg, I. A. Abrikosov, and S. I. Simak, Phys. Rev. B **87** (2013) 104111.
[2] O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys. Rev. B **84** (2011) 180301.
[3] W. Kohn and L. J. Sham, Phys. Rev. **140** (1965) A1133.
[4] D. Hobbs, G. Kresse and J. Hafner, Phys. Rev. B. **62** (2000) 11556.

Funded by the Emerging Frontiers in Research and Innovation (EFRI) program of the National Science foundation under grant # 1433467.

O.12 Finite temperature vibrational and thermal properties of Dichalcogenides

Antoine Dewandre[1,2], Matthieu Verstraete[1,2]

[1] *CESAM, Nanomat, ULiège, Belgium.*
[2] *European Theoretical Spectroscopy Facility* `www. etsf. eu`

Interest in the transition metal dichalcogenide materials has exploded due to their wide range of physical properties, which go from photovoltaic to thermoelectric applications. Dichalcogenides are also known to have a low out of plane thermal conductivity due to their layered structures. We present the vibrational and thermal properties of different Dichalcogenides,calculated using the Temperature Dependent Effective Potential package, linked as a library with Abinit, to calculate the finite temperature lattice dynamics. In particular we use an efficient automatic scheme for generating distorted snapshots which allows us to calculate anharmonic effects avoiding long ab-initio molecular dynamics runs.

O.13 The MULTIBINIT software project

Alexandre Martin[1], Jordan Bieder[2], Serguei Prokhorenko[1], Philippe Ghosez[1]

[1] *Theoretical Materials Physics, Q-MAT, CESAM, Université de Liège, B-4000 Liège, Belgium*
[2] *CEA DAM-DIF, F-91297 Arpajon, France*

Although extremely powerful, DFT calculations are still limited to relatively small systems and time-scales. The purpose of the MULTIBINIT project is to extend the capabilities of available first-principles codes in order to access the properties of mesoscale systems at operating conditions (i.e. at finite temperature and under external mechanical constraints or electric fields) in an automatic way and while retaining most of the first-principles predictive power and accuracy.

MULTIBINIT is an open software which implements the second-principles approach for lattice dynamics simulations based on atomic potentials fitted on first-principles calculations as proposed by Wojdel et al.[1]. It includes harmonic and anharmonic lattice parts as well as explicit treatment of homogeneous strains and their couplings to the lattice. The strength of the package is that it integrates efficient tools for (i) the generation of the model, (ii) the fit of the coefficients from first-principles data, (iii) finite temperature simulations and (iv) the post-process analysis of the results thanks to the AGATE software. The power of the method will be illustrated on systems such as ABO_3 perovskites.

[1] J.C. Wojdel, P. Hermet, M.P. Ljungberg, P. Ghosez and J. Íñiguez, First-principles model potentials for lattice-dynamical studies: general methodology and example of application to ferroic perovskite oxides, J. Phys.: Condens. Matter **25**, 305401 (2013)

O.14 Anharmonic Properties of Solids within the Stochastic Self-Consistent Harmonic Approximation: Phonons, Second-Order Structural Phase Transitions, and Thermal Properties

Ion Errea[1,2]

[1] *Fisika Aplikatua 1 Saila, Bilboko Ingeniaritza Eskola, University of the Basque Country (UPV/EHU), Bilbao, Basque Country, Spain*
[2] *Donostia International Physics Center (DIPC), Donostia-San Sebastián, Basque Country, Spain*

Describing atomic vibrations from first-principles accurately is of paramount importance to understand the thermodynamic and transport properties of solids. Phonon dispersions are routinely calculated within the harmonic approximation, and transport properties can be studied by estimating the electron-phonon and phonon-phonon interactions within perturbation theory. Nevertheless, whenever the amplitude of the atomic displacements largely exceeds the range in which the harmonic potential is valid, the harmonic approximation completely fails without allowing a perturbative expansion.

The stochastic self-consistent harmonic approximation (SSCHA) that we have developed[1,2] offers an efficient method to calculate vibrational properties of solids even when the harmonic approximation completely collapses. The method is variational and takes into account quantum and thermal effects rigorously. With our recent developments on the SSCHA method[3], we show how phonon frequencies should be defined from the second derivative of the free energy, which allows calculating the transition temperature of structural second-order phase transitions. Moreover, the new developments[3] allow calculating third-order anharmonic force-constants, which determine thermal properties, beyond the perturbative limit.

In this lecture we will present the method and several applications of it in superconducting hydrides, charge-density-wave systems, and thermoelectric materials.

[1] I. Errea, M. Calandra, and F. Mauri, Phys. Rev. Lett. **111** (2013) 177002.
[2] I. Errea, M. Calandra, and F. Mauri, Phys. Rev. B **89** (2014) 064302.
[3] R. Bianco, I. Errea, L. Paulatto, M. Calandra, and F. Mauri, Phys. Rev. B **96** (2017) 014111.

O.15 Anharmonic phonons and second-order phase-transitions by the stochastic self-consistent harmonic approximation

Raffaello Bianco[1,2], Ion Errea[3,4], Lorenzo Paulatto[5], Matteo Calandra[5], Francesco Mauri[1,2]

[1] *Graphene Labs, Fondazione Istituto Italiano di Tecnologia.*
[2] *Università di Roma "La Sapienza".*
[3] *University of the Basque Country (UPV/EHU).*
[4] *Donostia International Physics Center (DIPC).*
[5] *Université Pierre et Marie Curie (Paris VI), CNRS UMR 7590.*

Anharmonic effects can generally be treated within perturbation theory on top of the harmonic results. However, such an approach breaks down when the harmonic solution is dynamically unstable or when the anharmonic corrections to the phonon energies are larger than the harmonic frequencies themselves. Notably, this situation occurs near lattice-related second-order phase-transitions such as charge-density-wave (CDW) or ferroelectric instabilities or in H-containing materials, where the large zero-point motion of the protons results in a violation of the harmonic approximation. Interestingly, even in these circumstances, phonons can be observed, measured, and used to model transport properties. In order to treat such cases, we developed a method in the context of the stochastic self-consistent harmonic approximation (SSCHA) [1], devised to characterize, from first-principles, second-order displacive phase transitions and anharmonic phonons [2]. In particular, the method allows to analyze the evolution of the phonons spectrum and predict the transition point as a function of temperature (or any other appropriate parameter).

In this talk I will present the theoretical fundamentals of the method and its potential application to the analysis of displacive ferroelectric transitions, like in SnTe and GeTe; to the hydrogen-bond symmetrization transition occurring in the superconducting hydrogen sulfide system; to the CDW transitions occurring in 2D monolayer dichalcogenides, like in NbS_2, $NbSe_2$, and $TiSe_2$.

The authors acknowledge support from the Graphene Flagship. This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 696656 – GrapheneCore1

[1] I. Errea, M. Calandra, F. Mauri, Physical Review B, **89**, 064302 (2014)
[2] R. Bianco, I. Errea, L. Paulatto, M. Calandra, F. Mauri, Physical Review B, **96**, 014111 (2017)

O.16 Anharmonic phonon spectra of Mono and Dichalcogenides in the self-consistent harmonic approximation

Guilherme A. Ribeiro[1], Lorenzo Paulatto[1], Raffaello Bianco[2,3], Ion Errea[4,5], Francesco Mauri[2,3], Matteo Calandra[1]

[1] *Graphene Labs, Fondazione Istituto Italiano di Tecnologia.*
[2] *Università di Roma "La Sapienza".*
[3] *University of the Basque Country (UPV/EHU).*
[4] *Donostia International Physics Center (DIPC).*
[5] *Université Pierre et Marie Curie (Paris VI), CNRS UMR 7590.*

In this talk I will present applications of the stochastic self consistent approximation[1,2] to NbSe2[3] and to the monochalcogenides PbTe and SnTe[4]. NbSe2 is a layered two dimensional dichalcogenides displaying a charge density wave transition at 35 K and a superconducting transition at lower temperature. The charge density wave transition is suppressed applying a pressure of 4-5 GPa. In inelastic X-ray scattering, a strong temperature dependent soft phonon mode, reminiscent of the charge density wave (CDW), is found to persist up to a pressures as high as 16 GPa, far above the critical pressure at which the CDW disappears at 0 K. By using ab initio calculations beyond the harmonic approximation, we obtain an accurate, quantitative description of the Pressure v.s. temperature dependence of the phonon spectrum. Our results show that the rapid destruction of the CDW under pressure is related to the zero mode vibrations?or quantum fluctuations? of the lattice renormalized by the anharmonic part of the lattice potential. At room temperature, PbTe and SnTe are efficient thermoelectrics with a cubic structure. At low temperature, SnTe undergoes a ferroelectric transition with a critical temperature strongly dependent on the hole concentration, while PbTe is an incipient ferroelectric. By calculating anharmonic spectra with the stochastic self-consistent harmonic approximation, we find that vibrational spectra strongly depends on the exchange-correlation kernel used in density functional theory. Besides the well known LDA (GGA) tendency to overbind (underbind) inducing a volume error, the exchange and correlation error concerns also the accuracy in forces and total energies. If gradient corrections and the theoretical volume are employed, then the calculation of the free energy Hessian leads to phonon spectra in good agreement with experimental data for both systems. In PbTe, we reproduce the transverse optical mode phonon satellite detected in inelastic neutron scattering[5,6] and the crossing between the transverse optical and the longitudinal acoustic modes along the ΓX direction. In the case of SnTe we find that previous calculations [6] using temperature dependent phonon (TDEP) were substantially underconverged, resulting in larger anharmonic effects. After performing a careful convergence, we find that the occurrence of a ferroelectric transition from the high temperature Fm$\overline{3}$ structure to the low temperature R3m one is reproduced if using GGA. However, even if anharmonic phonon spectra are found to be in excellent agreement with experimental data, the ferroelectric transition is substantially underestimated in SnTe.

[1] I. Errea, M. Calandra and F. Mauri, Phys. Rev. Lett. **111**, 177002 (2013), Phys. Rev. B **89**, 064302 (2014)
[2] Raffaello Bianco, Ion Errea, Lorenzo Paulatto, Matteo Calandra and Francesco Mauri, Phys. Rev. B **96**, 014111 (2017)
[3] M. Leroux et al. Phys. Rev. B **92**, 140303(R) (2015)
[4] Ribeiro et al. `https://arxiv.org/abs/1709.03177`
[5] Delaire et al. Nature Materials **10**, 614-619 (2011)
[6] Li et al., Phys. Rev. Lett. **112**, 175501 (2014)

O.17 Phonon Anharmonicity near Lattice Instabilities: First-Principles Simulations and Scattering Experiments

Olivier Delaire

Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC, United States

A detailed understanding of anharmonic lattice dynamics is needed to refine microscopic theories of thermal transport and thermodynamics, and is of practical interest for the design of new functional materials. Lattice instabilities reveal strongly anharmonic phonons and impact numerous functional properties, such as ferroelectricity/multiferroicity or thermoelectricity. Furthermore, phonon-phonon interactions coexist with, and can be coupled to, electron-phonon interactions and renormalization of the electronic structure, as manifested across metal-insulator phase transitions. First-principles simulations of atomic dynamics now enable the rationalization of such effects and, in particular, ab-initio molecular dynamics simulations or anharmonic renormalization techniques at finite-temperature can capture striking effects of anharmonicity near lattice instabilities. Yet, newly developed simulation techniques need careful benchmarking against the most stringent experimental tests. Modern neutron and x-ray spectrometers have revolutionized our ability to map phonon spectral functions via the dynamical structure factor of single crystals, S(Q,E), throughout reciprocal space. This enables probing mode-resolved phonon scattering mechanisms, including anharmonicity, electron-phonon coupling, or scattering by defects and nanostructures. Such detailed experiments provide valuable input to assess modern simulations of phonon scattering and lattice instabilities. In this presentation, I will present results from our combined simulations and experiments of phonon transport in thermoelectric materials (PbTe, SnTe, AgSbTe2, SnSe) [1-4], ferroelectrics and multiferroics (SrTiO3, EuTiO3, YMnO3) [5], and of the metal-insulator transition in VO2 [6,7].

[1] O. Delaire, J. Ma, K. Marty, A. F. May, M. A. McGuire, M.-H. Du, D. J. Singh, A. Podlesnyak, G. Ehlers, M. Lumsden and B. C. Sales, Nature Materials **10**, 614 (2011).
[2] J. Ma*, O. Delaire*, A. F. May, C. E. Carlton, M. A. McGuire, L. H. VanBebber, D. L. Abernathy, G. Ehlers, Tao Hong, A. Huq, Wei Tian, V. M. Keppens, Y. Shao-Horn and B. C. Sales, Nature Nanotechnology **8**, 445 (2013).
[3] C.W. Li, O. Hellman, J. Ma, A.F. May, H.B. Cao, X. Chen, A.D. Christianson, G. Ehlers, D.J. Singh, B.C. Sales and O. Delaire, Physical Review Letters **112**, 175501 (2014).
[4] C.W. Li, J. Hong, A.F. May, D. Bansal, S. Chi, T. Hong, G. Ehlers and O. Delaire, Nature Physics **11**, 1063 (2015).
[5] D. Bansal, J. L. Niedziela, R. Sinclair, V. O. Garlea, D. L. Abernathy, S. Chi, Y. Ren, H. Zhou, and O. Delaire, *Momentum-resolved observations of the phonon instability driving geometric improper ferroelectricity in yttrium manganite*, in press.
[6] J. D. Budai, J. Hong, M. E. Manley, E. D. Specht, C. W. Li, J. Z. Tischler, D. L. Abernathy, A. H. Said, B. M. Leu, L. A. Boatner, R. J. McQueeney and O. Delaire, Nature **515**, 535-539 (2014).
[7] S. Lee, et al., Science **355**, 371 (2017)

Funding from US DOE, Office of Basic Energy Sciences, Materials Science and Engineering Division, through the Office of Science Early Career program, and as part of the S3TEC EFRC.

O.18 New directions for inelastic neutron scattering studies of anharmonic phonons

Brent Fultz

Dept. Applied Physics and Materials Science, mail 138-78, California Institute of Technology, Pasadena, CA 91125. USA.

For over 50 years, inelastic scattering experiments reported dispersion curves, $\omega(\vec{k})$, from single crystals, typically along high-symmetry directions of the crystal. These measurements were limited by the efficiency of instruments, low neutron flux, and challenges in managing data that would be obtained over more of k-space. Today these limitations are far less severe, and new types of measurements are possible.

Fermi chopper spectrometers at pulsed neutron sources are now measuring inelastic scattering at all $\vec{k}$ in a hundred or more Brillouin zones [1]. Traditional dispersion curves of phonons and magnons are nicely reproduced (see figure), but far more information is being acquired. The spectral weight of phonon excitations can now be measured with accuracy, revealing more information about anharmonic phonons. Phonon lineshapes can show more detail than just the symmetrical energy broadening expected from small anharmonicity. Measuring the spectral weight around phonon peaks offers new opportunities to explore strong anharmonicity where the quasiparticle description of phonons begins to lose validity.

I will give an example of a single crystal measurement on silicon to show the capabilities of the new measurements [2], and an example from cuprite to show unusual phonon spectral weights. For discussion, I will describe a different way to study the cubic anharmonicity by interference experiments. Key ideas of anharmonic interference were developed some years ago by Ambegaokar and others [3,4], who showed how phase relationships between phonons in three-phonon processes alter the spectral weights around single-phonon peaks. Could this be a useful probe of cubic anharmonicity?

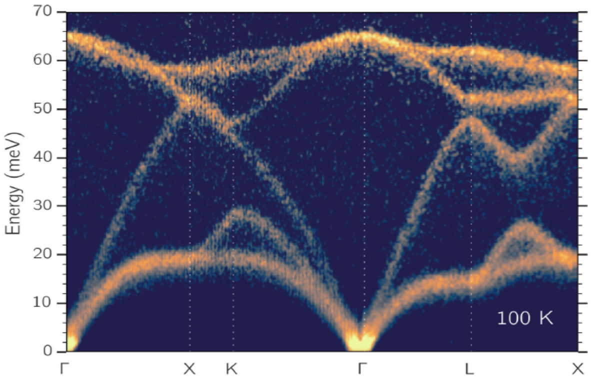


Figure O.3: Experimental phonon dispersions from silicon single crystal, acquired on the ARCS spectrometer at the SNS. Data were folded back into the first Brillouin zone.

[1] D. L. Abernathy, et al., Rev. Sci. Instrum. **83** (2012) 015114 (2012). doi: 10.1063/1.3680104

[2] D.S. Kim, et al., "A nuclear quantum effect with pure anharmonicity causes the anomalous thermal expansion of silicon," arXiv:1610.08737

[3] V. Ambegaokar, J. Conway, and G. Baym, in *Lattice Dynamics*, R.F. Wallis, ed., (Pergamon, New York 1965) p. 261.

[4] H.R. Glyde, Can. J. Phys. **52** (1974) 2281.

O.19 Testing models of heat transport using high hydrostatic pressure and anharmonicty of lattice vibrations

David G. Cahill[1]

[1] *Department of Materials Science and Engineering,*
Materials Research Laboratory
University of Illinois, Urbana IL, USA

The combination of anharmonic lattice vibrations and the high hydrostatic pressure environments provided by diamond anvil cells enables elegant tests of models for the materials physics of heat conduction,[1] and the thermal conductance of interfaces.[2,3] Time-domain thermoreflectance (TDTR) is a modulated pump-probe optical technique based on an ultrafast model-locked laser as the light source. We model the data and extract thermal transport coefficients using exact solutions of the diffusion equation in an arbitrary multilayer geometry, where each layer can have a tensor thermal conductivity. Despite the complexity of the atomic and molecular vibrations of an amorphous polymer, the pressure dependence predicted by the model of the minimum thermal conductivity is in excellent agreement with data for PMMA[1] to 12 GPa. The pressure dependence of clean and graphene-modified interfaces between Al and SiC reveal the strong dependence of interface thermal conductance on the stiffness of interfacial bonds,[2] see Fig. O.4. The mechanisms that produce anomalously high thermal conductance at interfaces between highly dissimilar materials (e.g., Pb/diamond), have remained unresolved for 30 years. The pressure dependence of the thermal conductance of interfaces of metals with diamond suggest a three-phonon channel for heat conduction involving two-phonons in diamond and one phonon in the metal.[3]

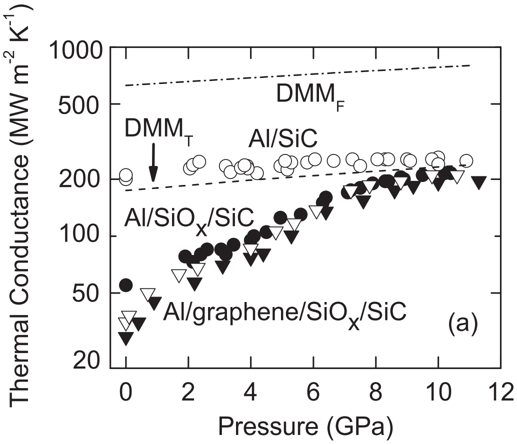


Figure O.4: Pressure dependence of the thermal conductance $G(P)$ of various Al/SiC interfaces. $G(P)$ of the weak interfaces Al/SiO$_x$/SiC (solid circles) and Al/graphene/SiO$_x$/SiC (open and solid triangles) increases rapidly with pressure due to the increasing interface stiffness and approaches the value of the clean Al/SiC interface at $P > 8$ GPa. The diffuse-mismatch-model (DMM) prediction of $G(P)$ of the Al/SiC interface is shown as the dashed line for the truncated model (DMMT) and as a dashed-dot line for the full Debye model (DMMF).

[1] W.-P. Hsieh *et al.*, Phys. Rev. B **83** (2011) 174205.
[2] W.-P. Hsieh *et al.*, Phys. Rev. B **83** (2011) 184107.
[3] G. T. Hohensee *et al.*, Nat. Commun. **6** (2015) 6578.

O.20 Investigation of phonon states in a poor thermal crystalline conductor by means of inelastic scattering spectroscopy

Stéphane Pailhès[1]

[1] *Institute of Light and Matter, CNRS, UCBL, UMR-5586, 69622 Villeurbanne, Lyon, France*

The modeling of thermal transport in dielectrics and semiconductors requires the knowledge of the phonon states in the phase space ($\mathbf{q}$,$\hbar\omega$) and as a function of temperature. Their experimental investigation, and more specifically, that of the anharmonicity which limits their lifetime and is responsible for the thermal resistance, is essential for the theoretical development. However, while phonon energies are experimentally mastered properties, the measurement of phonon lifetime turns out to be difficult even in simple systems.

In this talk, we will present the neutrons and X-rays spectroscopy techniques currently used for measuring thermal phonon energies, specifically illustrating their technical limitations, which have prevented until now any measurement of phonons lifetime in most crystals *[1]*. We will focus on the phonon dynamics in clathrates, a family of materials with complex crystal unit cell renowned for their puzzling low ($\sim$ 1-2 W.m^{-1}.K^{-1} at 300 K) and almost temperature independent thermal conductivity. Here, we present the first measurement of phonon lifetimes in a clathrate single crystal with composition $Ba_{7.81}Ge_{40.67}Au_{5.33}$ *[2]*. Fig. O.5 *(left)* reports the mapping of the scattered intensity in the phase space in the transverse polarization, which reveals the dispersion of transverse acoustic phonons over a full Brillouin Zone (BZ). Fig. O.5 *(right)* reports the corresponding lifetime, measured for the first time thanks to the Neutron Resonant Spin-Echo technique (NRSE). Surprisingly, we find acoustic phonons with long lifetimes, traveling over distances from a hundred to tens of nanometers as their wave-vectors increase towards the boundary of the BZ. This finding challenges the common belief that low thermal conductivity implies short mean free paths. This apparent contradiction can be reconciled within the simple kinetic theory of thermal transport if only the low energy acoustic phonons are considered.

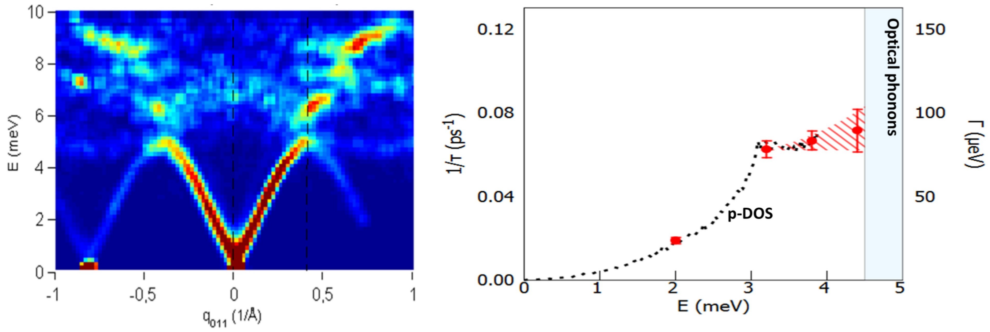


Figure O.5: *(Left)* Experimental mapping of the transverse acoustic phonons in $Ba_{7.81}Ge_{40.67}Au_{5.33}$ measured at 300 K by means of neutron time-of-flight(IN5@ILL) *(Right)* Energy dependence of the inverse lifetimes (left) or spectral width (right) of these phonons as determined by neutron resonant spin-echo (IN22@ILL)

[1] S. Pailhès et al., Chapter **19** in book " Nanostructured Semiconductors - Amorphization and Thermal Properties", Ed. K. Termentzidis, Pan Stanford (2017)
[2] P.F. Lory et al., Nat. Comm. **8**,491 (2017)

O.21 Temperature dependence of the electronic structure : the direct and indirect roles of phonons

Xavier Gonze[1]

[1] *Institute of condensed matter and nanoscience, UCLouvain, 8 chemin des étoiles, B-1348 Louvain-la-neuve.*

Modifications of electronic eigenenergies due to vibrational effects and electron-phonon coupling are sizable in many materials, even at zero temperature for materials with light atoms: phonon occupation numbers varies with temperature, and electron-phonon coupling propagates such variation to the electronic structure. Also the thermal expansion might have an indirect effect on the electronic structure.

While often neglected in first-principles calculations, the direct modifications due to electron-phonon coupling have been recently obtained using different formalisms, among which the perturbation-based Allen-Heine-Cardona (AHC) approach, considering both the adiabatic and the non-adiabatic harmonic approximation. Electron-phonon coupling can be obtained from density-functional perturbation theory (DFPT) as well as from many-body perturbation theory (MBPT), e.g. the GW approximation.

I will provide a brief overview of the concepts and formalisms, and present recent progresses, including : the validation of AHC theory implementation in two different software applications, with an agreed DFPT zero-point motion correction of 0.4 eV for the direct bandgap of diamond[1] ; the MBPT result for the same material, 40% higher[2]; the breakdown of the adiabatic AHC theory for infrared-active materials, and fix of this problem in the non-adiabatic AHC theory[3,4]. The electronic structure is also modified by the thermal expansion, that can be obtained within the quasi-harmonic approximation. For several materials, the thermal expansion effect on electronic structure is much smaller than the direct phonon occupation variation, but not always. In view of a recent paper[5], I will also revisit the quasi-harmonic approximation and show how it can fail for the temperature dependence of the electron and phonon energies, still being perfectly valid to predict the thermal expansion.

[1] S.Poncé, G. Antonius, P. Boulanger, E. Cannuccia, A. Marini, M. Côté and X. Gonze, Computational Materials Science **83** (2014) 341.
[2] G. Antonius, S. Poncé, P. Boulanger, M. Côté and X. Gonze, Phys. Rev. Lett. **112** (2014) 215501.
[3] S. Poncé, Y. Gillet, J. Laflamme Janssen, A. Marini, M. Verstraete and X. Gonze, J. Chem. Phys. **143** (2015) 102813.
[4] G. Antonius, S. Poncé, E. Lantagne-Hurtubise, G. Auclair, X. Gonze and M. Côté, Phys. Rev. B **92** (2015) 085137.
[5] D.S. Kim *et al.* `https://arxiv.org/abs/1610.08737`

O.22 Device physics repercussion of semiconductor anharmonicity: halide perovskites

Jarvist Moore Frost[1,2], Lucy D. Whalley[2], Jonathan Skelton[1], Aron Walsh[1,3]

[1] *Department of Chemistry, University of Bath, UK.*
[2] *Department of Materials, Imperial College London, UK.*

Halide perovskites are soft, polar, semiconductors[1]. Anharmonicity in the phonon modes leads to extremely low thermal conductivity[2]. Strong dielectric electron-phonon coupling leads to correlated electron and phonon degrees of freedom, the formation of a polaron.

We can describe this interacting system with path integrals, integrating out the (infinite) degrees of freedom associated with the phonon quantum field. We have recently implemented codes to calculate the finite-temperature Feynman polaron state, parametrised by a Fröhlich dielectric electron-phonon coupling[3,4]. For a polar material, this long-range coupling can be expected to dominate the electron-phonon interaction. This model provides temperature dependent charge carrier mobilities, with no free parameters. For halide perovskite systems, the predictions agree well with experiment, indicating that we are capturing the essential physics.

From a characterisation of this finite-temperature polaron state, we have proposed a model for the observed slow carrier cooling in halide perovskites[5]. The polaron state is stable at high temperature, and results in a limited density of states which the hot-electron is in thermal contact with. The very low lattice thermal conductivity retains the localisation of this transient hot-spot.

One of the most simple theories for electron-phonon coupling is that of the deformation potential, where an adiabatic separation is made of the electron and nuclear degrees of freedom. Double-well potentials, associated with symmetry-breaking distortions, are an important source of soft anharmonic potentials. As an application we look at the zone-boundary tilt modes in halide perovskite semiconductors.

By distorting along the soft eigenvector of the dynamic matrix, an approximate one-dimensional potential energy landscape can be explored. On this potential energy landscape, we can solve a (trivial in one dimension) Schrödinger equation for the collective nuclear degree of freedom. From the resulting complete set of athermal states, a thermodynamic ensemble (with either Bose-Einstein or Boltzmann populations) can be constructed. By convolving the temperature-dependent probability density function of this ensemble with the band gap deformation potential, a temperature-dependent electron-phonon coupling can be calculated for arbitrary (soft; anharmonic) modes[2].

From another point of view we can model quantum nuclear effects with path integrals. The Feynman-Kleinert[6] variational method replaces a bare classical potential with an effective potential, to reproduce as close as possible the true quantum partition function. This is again trivial in one dimension. We apply it to double-well potential systems.

[1] JM Frost and A Walsh. Acc.Chem.Res. 49 (3) pp 528–535 (2016).
[2] LD Whalley, JM Skelton, JM Frost, and A Walsh. Phys. Rev. B 94, 220301(R) (2016).
[3] JM Frost. ArXiv:1704.05404 (2017), PRB in press.
[4] `https://github.com/jarvist/PolaronMobility.jl`
[5] JM Frost, L Whalley and A Walsh. ACS Energy Letters (2017).
[6] R. P. Feynman and H. Kleinert. Phys. Rev. A 34, 5080.

O.23 Phonons properties of two temperature metals

Vanina Recoules, François Bottin, Johann Bouchet

CEA/DAM-DIF, 91297 Arpajon, Cedex, France.

Ultrashort laser pulses excite electrons, which thermalize to temperatures of several eV within a few femtoseconds. In contrast, the ionic lattice is unaffected on the time scale of the laser pulse. The energy transfer from the hot electrons to the ionic degrees of freedom is a slower process and a new equilibrium temperature is not reached before several picoseconds have passed. This ultrafast energy absorption by electrons and the finite rate of their energy transfer to the lattice creates non-equilibrium states of matter refered as two-temperature system with hot electrons and an ionic lattice at low temperature.

The effect of this intense electronic excitation on the interatomic forces was studied using ab initio linear response to compute the phonon spectrum for metals with electronic temperatures up to 6eV [1,2]. Metals properties, as for example melting temperature or elastic constants, are strongly modified and these modifications depend on the metals considered. All these calculations only describe the effect of the increase of electrons temperature, but the increase of the ions temperature is still poorly understood. The prospect of extracting phonon spectrum and derived properties directly from two-temperature ab initio molecular dynamics simulation is then very appealing. This was done using the TDEP module developed the ab initio plane wave Density Functional Theory (DFT) code Abinit [3]. For non-equilibrium molecular dynamics simulations, the ion and electron temperatures are controlled independently. The electron temperature is controlled by the width of the Fermi-Dirac distribution. The ion temperature is controlled in the iso-kinetics ensemble where the velocity are rescaled at every time step to maintain the desired ionic temperature. The first results will be shown for aluminum, molybdenum and gold.

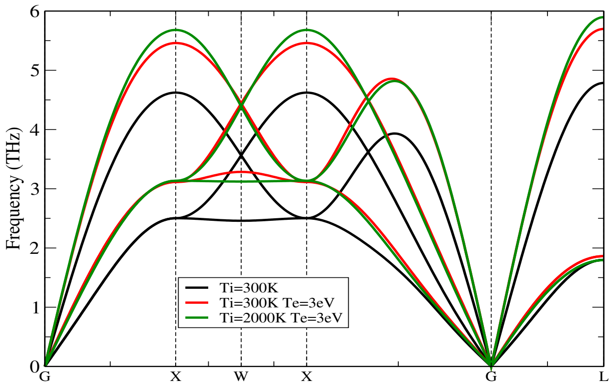


Figure O.6: Phonon spectra for gold.

[1] V. Recoules, J. Clérouin, G. Zérah, P.M. Anglade, S. Mazevet, Phys. Rev. Lett.**96** (2006) 055503.

[2] F. Bottin and G. Zerah, Phys. Rev. B **75** (2007) 174114.

[3] F. Bouchet and F. Bottin, Phys. Rev. B **92** (2015) 174108.

O.24 Extreme anharmonicity in metal-organic frameworks: challenges and opportunities

Aron Walsh

Department of Materials, Imperial College London, UK

Metal-organic frameworks (MOFs) are porous ordered arrays of inorganic clusters supported by organic linking units. They have attracted attention for gas storage, separation and catalysis, which rely on weak chemical bonding with a molecular absorbate. The recent focus has shifted to physical responses, with examples of semiconducting and metallic compounds [1]. I will discuss progress in the understanding of the vibrational properties of hybrid frameworks.

Our recent work has included analysing the effect of anisotropic thermal expansion on magnetic exchange interactions in a cobalt adipate framework within the quasi-harmonic approximation [2], probing thermal motion and its effect on lattice polarisation in metal formate perovskites from quasi-harmonic and molecular dynamic simulations [3], as well as probing large thermal displacements of ligands with rotational freedom [4].

The combination of light and heavy building chemical blocks with mechanical softness results in a complex vibrational landscape for hybrid frameworks (Figure 1). There are cases of giant negative thermal expansion, and vibrational entropy is seen as a key descriptor of phase stability and transformations [5]. I will address a range of theoretical approaches to describe the internal dynamics of these materials including rotational-vibrational behaviour of molecular units inside deformable cage structures. We have been developing practical approaches for dealing with anharmonic potential energy surfaces in complex materials such as these [6]; however, further extensions in theory and methodology are necessary.

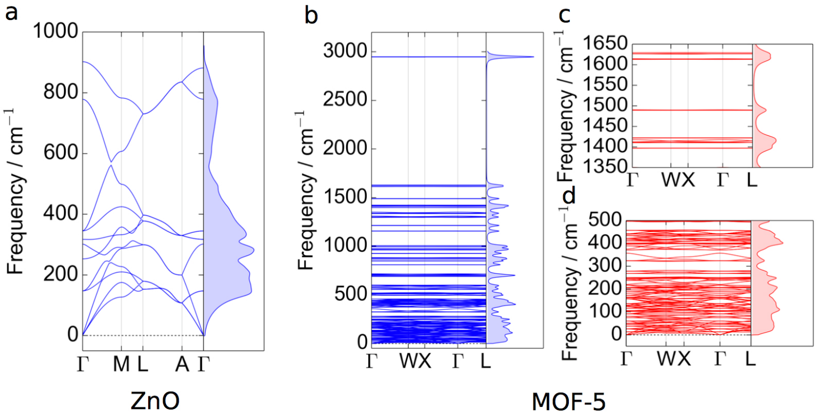


Figure O.7: Phonon dispersion in (a) ZnO and (b,c) the ZnO-containing framework, MOF-5.

The results reported in this presentation have been performed by group members including Katrine Svane, Jonathan Skelton, Keith Butler, and Jessica Bristow.

[1] A. Walsh, C. H. Hendon and K. T. Butler, MRS Bulletin **41** (2016) 870.
[2] K. L. Svane, P. Saines and A. Walsh, J. Mater. Chem. C **3** (2015) 11076.
[3] K. L. Svane and A. Walsh, J. Phys. Chem. C **121** (2017) 421.
[4] K. L. Svane, J. K. Bristow and A. Walsh, J. Phys. Chem. C **121** (2017) 22010.
[5] K. T. Butler et al, Chem. Sci. **7** (2016) 6316.
[6] J. M. Skelton et al, Phys. Rev. Lett. **117** (2016) 075502.

O.25 Coherent phonon dynamics in bismuth: A quantitative study of phonon-phonon and electron-phonon coupling

Brice Arnaud[1]

[1] *Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans université, 72085 Le Mans Cedex*

The semi-metal bismuth exhibits many fascinating properties, such as giant magnetoresitance, thermoelectricity and large diamagnetism. The possibility to drive bismuth strongly out of equilibrium by an ultrashort laser pulse and especially to launch optical and acoustic coherent phonons has renewed the interest for bismuth that can now be seen as a test material in the field of ultrafast physics.

The ultrafast lattice dynamics in bismuth can be tackled from first principles provided that some equilibrium properties are correctly described at the density functional theory (DFT) level and that a mean to describe a transient non-equilibrium situation is found. We computed the elastic constants of bismuth using a finite strain approach and the thermal expansion coefficients using the quasi-harmonic approximation. We found an overall good agreement with experiments[1]. We also computed the lifetime of the A_{1g} optical phonon and made a detailed comparison with Raman measurements performed for different temperatures.

In order to simulate the time evolution of the coherent A_{1g} phonon launched by an ultrashort laser pulse, we introduced a thermodynamical model based on the two-temperature approach[2]. This model provides a good description of time-resolved X-ray diffraction experiments[3] and shows that the electronic entropy governs the dynamic of the coherent phonon. We also demonstrated that the effective electron-phonon coupling constant governing the electron cooling in laser-excited bismuth depends strongly on the electron temperature[4]. The theoretical description of the coherent phonon lifetime[5] that depends strongly on the laser fluence is currently investigated.

[1] B. Arnaud, S. Lebègue and G. Raffy, Physical Review B **93**, 094106 (2016)
[2] Y. Giret, A. Gellé and B. Arnaud, Phys. Rev. Lett. **106**, 155503 (2011).
[3] D.M. Fritz *et al*, Science **3**15, 633 (2007).
[4] B. Arnaud and Y. Giret, Phys. Rev. Lett. **110**, 016405 (2013).
[5] S. Fahy, E. D. Murray, and D. A. Reis, Phys. Rev. B **93**, 134308 (2016).

O.26 Achieving high thermal conductivity from weak anharmonic phonon scattering

David Broido[1], Navaneetha Krishnan Ravichandran[1], Nakib Protik[1], Chunhua Lee[1]

[1] *Department of Physics, Boston College, Chestnut Hill, MA, USA.*

The intrinsic thermal conductivity of a nonmetallic crystal is limited by phonon-phonon scattering arising from the anharmonicity of the interatomic potential. Over the past several decades, many materials have been studied that have low thermal conductivity. These include the highly anharmonic crystals such as Bi_2Te_3 and PbTe, which are useful materials for thermoelectrics. In contrast, little progress has been made in identifying new high thermal conductivity materials. By far the best thermal conductor for applications is diamond, which achieves its high thermal conductivity through its harmonic properties i.e. stiff covalent bonds and light atomic masses. However, diamond is scarce and difficult to fabricate synthetically.

Recently, we have proposed a new paradigm for achieving high thermal conductivity in nonmetallic crystals.[1] The approach involves tailoring the vibrational properties to reduce the phase space for three-phonon scattering, which is the lowest order anharmonic scattering process. One material, cubic Boron Arsenide (BAs), has been predicted to have room temperature thermal conductivity $>$ 2000 W/m-K, comparable to that of diamond.

In this talk, I will address the multitude of material constraints that must be satisfied in order to achieve high thermal conductivity with the new paradigm. These include (i) a large frequency gap between acoustic and optic phonons, (ii) bunching together of acoustic phonon branches, (iii) weak scattering of phonons by defects (e.g. isotopes, vacancies), (iv) small bandwidth of optic phonons, (v) weak phonon scattering from higher-order anharmonicity (four-phonon scattering), and (vi) weak electron-phonon scattering in metallic crystals . I will discuss our *ab initio* calculations to examine these constraints individually and collectively.

[1] L. Lindsay, D. A. Broido and T. L. Reinecke, Phys. Rev. Lett. **111** (2013) 025901.

Supported by the National Science Foundation under Grant No. 1402949 and by the ONR Multi-University Research Intiative Grant No. N00014-16-1-2436.

O.27 Phonon diffraction and dimensionality crossover in phonon-interface scattering

Riley Hanus[1], Anupam Garg[2], G. Jeff Snyder[1]

[1]*Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA.*
[2]*Physics and Astronomy, Northwestern University, Evanston, IL 60208, USA.*

This theoretical work provides several mechanistic understandings of phonon-interface scattering. The treatment provided here defines the interface as an array of linear defects, as opposed to a structureless planar defect which is inherent in current models. This is the basis on which prevailing models for the structure and energy of interfaces are grounded, and we extend this definition to phonon-interface scattering. We apply the analytical expression derived here to phonon-GB strain field scattering from a symmetric tilt grain boundary. It is shown that phonon diffraction conditions arise from the periodic nature of these defect arrays as can be expected from the wave-like nature of phonons. Furthermore, for diffuse heat conduction, a dimensionality crossover is observed in the frequency (ω) dependence of the scattering rate which arrises from phase space considerations. This crossover in defect dimensionality provides a mechanistic understanding for ω-dependence in phonon-interface scattering, transmissivity, specularity, and the T^2 behavior in the low temperature lattice thermal conductivity of polycrystalline and nanocrystalline materials.

O.28 Thermal properties of PbTe and GeTe based materials near ferroelectric phase transition

Ronan Murphy[1,2], Djordje Dangić[1,2], Éamonn Murray[3], Stephen Fahy[1,2], Ivana Savić[1]

[1] *Tyndall National Institute, Dyke Parade, Cork, Ireland*
[2] *Department of Physics, University College Cork, College Road, Cork, Ireland*
[3] *Departments of Physics and Materials, Imperial College London, London SW7 2AZ, UK*

Accurate modelling of thermal properties of materials near structural phase transitions requires an explicit account of temperature effects on phonon frequencies [1]. In this talk, however, I will illustrate a few examples where using phonon frequencies and lifetimes calculated from 0 K interatomic force constants can successfully reproduce several measurements of vibrational and thermal properties of ferroelectric GeTe and incipient ferroelectric PbTe. First I will show that, by using the harmonic approximation and explicitly accounting for the temperature dependence of elastic constants, we can obtain the temperature variation of the structural parameters of GeTe in very good agreement with experiment [2]. Then I will show that we can reproduce the two-phonon spectrum of photoexcited PbTe measured by ultrafast diffusive X-ray scattering using phonon frequencies and lifetimes obtained from 0 K forces [3]. Finally, I will argue that the same approach gives correct qualitative trends for the lattice thermal conductivity of PbTe and (Pb,Ge)Te alloys as they are driven very near the phase transition [4,5].

[1] A. H. Romero, E. K. U. Gross, M. J. Verstraete, and O. Hellman, Phys. Rev. B **91** (2015) 214310.
[2] Dj. Dangić, R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, in preparation.
[3] M. P. Jiang, M. Trigo, I. Savić *et al.*, Nature Commun. **7** (2016), 12291.
[4] R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B **93** (2016) 104304.
[5] R. M. Murphy, É. D. Murray, S. Fahy, and I. Savić, Phys. Rev. B **95** (2017) 144302.

O.29 Thermal properties of bismuth and bismuth nanostructures calculated ab initio.

Jelena Sjakste[1], Maxim Markov[1], Giorgia Fugallo[1], Lorenzo Paulatto[2], Michele Lazzeri[2], Francesco Mauri[3], Nathalie Vast[1]

[1] *École Polytechnique, Laboratoire des Solides Irradiés, CNRS UMR 7642, CEA-DSM-IRAMIS, Université Paris-Saclay, F91128 Palaiseau cédex, France,*
[2] *IMPMC, UMR CNRS 7590, Sorbonne Universités - UPMC Univ. Paris 06, MNHN, IRD, 4 Place Jussieu, F-75005 Paris, France,*
[3] *Dipartimento di Fisica, Università di Roma La Sapienza, Piazzale Aldo Moro 5, I-00185 Roma, Italy.*

In this talk we will present our recent results of the ab initio calculations of thermal transport properties in bismuth and bismuth nanostructures [1]. We have employed the recently developed methods of the solution of Boltzmann transport equation and phonon-phonon matrix elements calculation [2,3].

We have first obtained the temperature dependence of the bulk lattice thermal conductivity of Bi in excellent agreement with available experiments. Surprisingly, we find that the coupling between accoustical and optical phonons strongly influences the thermal conductivity in Bi, thus explaining the discrepancy between experimental results and previous ab initio calculations [1,4]. We have also considered heat transport in polycrystalline thin films of Bi. The calculated lattice thermal conductivity is found in excellent agreement with the available experimental data [1].

In the second part of this talk, we will discuss the occurrence of the hydrodynamic heat transport regime in bismuth [5]. Bismuth is one of the rare materials in which second sound has been experimentally observed. Our calculations predict the occurrence of the Poiseuille phonon flow in Bi between ≈ 1.5 K and ≈ 3.5 K for sample size of 3.86 mm and 9.06 mm, in consistency with the experimental observations [6]. We will also discuss a Gedanken experiment allowing to assess the occurrence of the hydrodynamic regime in any bulk material.

[1] M. Markov, J. Sjakste, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, N. Vast, Phys. Rev. B **93**, 064301 (2016).
[2] L. Paulatto, F. Mauri, M. Lazzeri, Phys. Rev. B **87**, 214303 (2013).
[3] G. Fugallo, M. Lazzeri, L. Paulatto, F. Mauri, Phys. Rev. B **88**, 045430 (2013).
[4] S. Lee, K. Esfarjani, J. Mendoza, M. S. Dresselhaus, G. Chen, Phys. Rev. B **90**, 195438 (2014).
[5] M. Markov, J. Sjakste, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, N. Vast, 2017, submitted.
[6] V. Narayanamurti and R.C. Dynes, Phys. Rev. Lett. **28**, 1461, (1972).

O.30 Ab-initio thermal properties of semiconductors with higher order anharmonicities

Navaneetha Krishnan Ravichandran[1], David Broido[1]

[1] *Boston College, Chestnut Hill, MA, USA.*

The thermal properties of semiconductors are affected by the anharmonicity of the interatomic crystal potential. In many semiconductors, inclusion of harmonic and third-order anharmonic processes involving three phonons are sufficient in accurately reproducing measured thermal properties, such as specific heat, thermal expansion and thermal conductivity. However, in highly anharmonic materials, higher-order anharmonicities and higher-order phonon processes can become important, particularly at high temperatures, and play a role in determining the equilibrium structure, and thermal and thermodynamic properties [1, 2, 3, 4]. Furthermore, materials such as BAs have an unusually weak 3-phonon scattering phase space, which results in exceptionally high calculated 3-phonon limited k_L comparable to that of diamond at room temperature [5]. Thus, even in weakly anharmonic materials such as BAs, higher order 4-phonon scattering processes can significantly affect their thermal properties, if the 4-phonon scattering phase space is sufficiently strong.

In this talk, we describe an approach to calculate the ab-initio thermal properties of semiconductor materials, in which up to fourth order anharmonicity in the crystal potential is included and different types of energy and momentum conserving three and four phonon processes correct to first and second orders in perturbation theory are considered. In our approach, we explicitly include third and fourth order contributions to the free energy to predict the equilibrium lattice parameters from first principles. At these equilibrium lattice parameters, we evaluate three- and four-phonon contributions to the thermal and thermodynamic properties such as specific heat, thermal expansion, phonon line shapes and thermal conductivity. To evaluate the anharmonic interatomic force constants (IFCs) required to calculate the three- and four-phonon scattering cross sections, we explicitly include the effects of temperature, zero-point motion and long range electrostatic interactions of atoms on the IFCs. To mitigate the significant computational cost associated with the evaluation of higher order phonon processes, we rigorously incorporate various symmetry and invariance relations on the third and fourth order IFCs, and on the three- and four-phonon scattering matrix elements in our calculations. By evaluating higher order anharmonic contributions to free energy, phonon line shifts and line widths, our work will inform accurate prediction of crystal stability, neutron scattering cross-sections and thermal conductivity of several challenging anharmonic semiconductor crystals, and help identify new novel materials with unique thermal and thermodynamic properties.

[1] O. Hellman et al., Phys. Rev. B **87**, 104111 (2013)
[2] D. Kim et al., `https://arxiv.org/abs/1610.08737` (2017)
[3] O. Delaire et al., Nat. Materials **10**, 614-618 (2011)
[4] T. Feng et al., Phys. Rev. B **93**, 045202 (2016)
[5] L. Lindsay et al., Phys. Rev. Lett., **111**, 025901 (2013)

O.31 High-throughput finite-temperature properties of oxide and fluoride perovskites

Ambroise van Roekeghem[1], Jesús Carrete[1,2], Corey Oses[3],
Stefano Curtarolo[3,4] and Natalio Mingo[1]

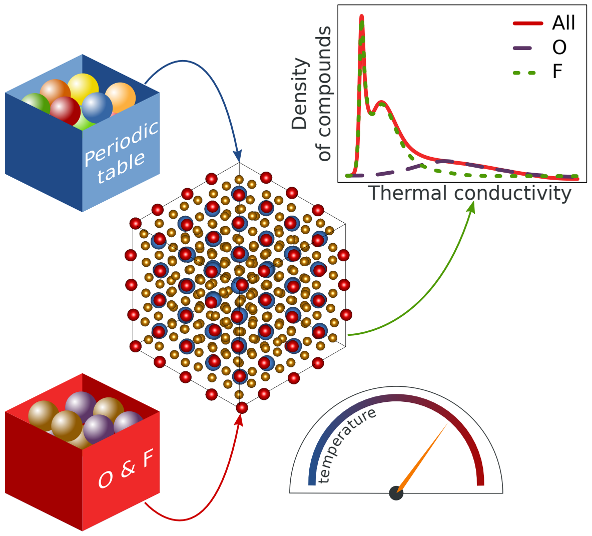
[1] *CEA, LITEN, 17 Rue des Martyrs, 38054 Grenoble, France*
[2] *Institute of Materials Chemistry, TU Wien, A-1060 Vienna, Austria*
[3] *Center for Materials Genomics, Duke University, Durham, NC 27708, USA*
[4] *Materials Science, Electrical Engineering, Physics and Chemistry, Duke University, Durham, NC 27708, USA*

Using finite-temperature phonon calculations, we calculate the mechanical stability of about 400 semiconducting oxides and fluorides with cubic perovskite structures, at 0 K, 300 K and 1000 K. We find 92 mechanically stable compounds at high temperatures – including 36 not mentioned in the literature so far – for which we calculate the thermal conductivity.

We demonstrate that the thermal conductivity is generally smaller in fluorides than in oxides, largely due to a lower ionic charge, and describe simple structural descriptors that are correlated with its magnitude.

Furthermore, we show that the thermal conductivities of most cubic perovskites decrease more slowly than the usual T^{-1} behavior.

Finally, we describe a strategy to accelerate the discovery of mechanically stable compounds at high temperatures, and some simple approximations to obtain temperature-dependent static dielectric constants and electronic mobilities in those compounds.



[1] A. van Roekeghem, J. Carrete, C. Oses, S. Curtarolo and N. Mingo, Phys. Rev. X **6** (2016) 041061.
[2] A. van Roekeghem, J. Carrete, S. Curtarolo and N. Mingo, in preparation.

O.32 Predicting the lattice thermal conductivity of transition metal oxides and inorganic-organic superlattices with dispersion-corrected hybrid density functional methods

Antti Karttunen[1], Jarno Linnera[1], and Nina Glebko[1]

[1] *Department of Chemistry and Material Science, Aalto University, Finland*

Controlled manipulation of heat flows at the atomic level is a major goal in the fields of energy materials and electronics. We have recently investigated the atomistic thermal engineering of several thermoelectric material families that have potential for direct heat-to-electricity conversion. In practice, we combine Density Functional Theory (DFT) calculations with Boltzmann Transport Equation (BTE) for phonons, as implemented in Phono3py[1] and ShengBTE[2].

Transition metal oxides based on abundant and non-toxic metals are an appealing starting point for atomistic thermal engineering towards more efficient thermoelectric materials. However, $3d$ transition metal oxides such as Cu_2O are known to be a challenging case for DFT-GGA. We have interfaced the Phono3py code with the CRYSTAL code to enable efficient hybrid DFT+BTE calculations. At 300 K, hybrid DFT-PBE0 overestimates the lattice thermal conductivity of Cu_2O only by 5%, while DFT-PBE underestimates it by 44% (Figure O.8).[3]

The thermoelectric efficiency of bulk metal oxides is reduced by too high thermal conductivity. Our recent combined experimental–computational energy materials research has focused on thermal engineering of ZnO via fabrication of hybrid oxide–organic superlattices (Figure O.8).We carried out DFT+BTE studies for both ZnO and ZnO–organic superlattices using ShengBTE and Quantum Espresso, and showed that so-called cumulative lattice thermal conductivity is a simple but effective tool to design thermoelectric oxide–organic superlattices.[4]

The further extension of the atomistic thermal engineering approach to layered $3d$ transition metal sulfides and related hybrid materials requires the application of dispersion-corrected DFT methods. We have investigated TiS_2, ZrS_2, and HfS_2 with DFT-PBE0-D3+BTE calculations and discuss the effect of the dispersion corrections on the lattice thermal conductivity.

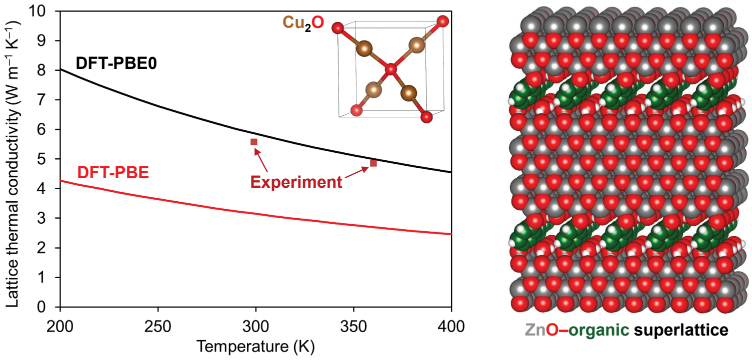


Figure O.8: Left: Lattice thermal conductivity of Cu_2O obtained with DFT-PBE0 and DFT-PBE methods (Phono3py/CRYSTAL). Right: ZnO-organic superlattice (period 1.2 nm).

[1] A. Togo, L. Chaput, and I. Tanaka, Phys. Rev. B**91** (2015) 094306.
[2] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comput. Phys. Comm. **185** (2014) 1747.
[3] J. Linnera and A. J. Karttunen, Phys. Rev. B **96** (2017) 014304.
[4] A. J. Karttunen, T. Tynell, and M. Karppinen, Nano Energy **22** (2016) 338.

O.33 Breaking periodicity: vibrations of defects in photovoltaic materials

Lucy D. Whalley, Jarvist Moore Frost and Aron Walsh

Department of Materials, Imperial College London, UK

For a crystalline solid above room temperature point defects are unavoidable. Although there has been extensive research investigating the effect of defects upon the electronic properties of semiconducting materials, less is known about the effect upon vibrational properties.

We know that breaking translational symmetry with a defect will result in localised or quasi-localised (resonant) vibrational states [1]. These states are related to flattened dispersions in the phonon spectrum and can reduce the thermal conductivity of the material depending upon the defect concentration and distribution. They may also allow for multi-phonon capture, allowing the defect to become a site for non-radiative recombination - a 'killer' defect in the context of photovoltaic devices.

We will present results from finite-displacement calculations on defective supercells using the `Phonopy` open source package. The material of interest is methylammonium lead iodide, a highly anharmonic hybrid perovskite with strong phonon-phonon interactions, large thermal displacements and ultra-low thermal conductivity [2]. Building upon a classification scheme introduced by Hayes and Stoneham [1], we will quantify the localisation of defect vibrations using the Inverse Participation Ratio and discuss the consequences for non-radiative recombination of photo-generated electrons and holes.

[1] W. Hayes and A. M. Stoneham, "Defects and Defect Processes in Nonmetallic Solids", Dover (1985).
[2] L. D. Whalley, J. M. Skelton, J. M. Frost and A. Walsh, Phys. Rev. B **94** (2016) 220301(R).

O.34 Novel high-entropy carbides discovered by synthesizability descriptors

Stefano Curtarolo[1,2]

[1] *Materials Science, Electrical Engineering, Physics and Chemistry, Duke University, Durham NC, 27708, USA*

[2] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin-Dahlem, Germany*

High-entropy materials have attracted considerable interest due to their combination of potentially unique properties and promising technological applications. Predicting their formation from previously known parameters remains the major hindrance to the discovery of new systems. In this seminar, we introduce a descriptor - entropy forming ability - for predicting the synthesizability of such systems from first principles calculations. The formalism, based on the energy distribution spectrum of randomized calculations, captures the accessibility of equally-sampled states near the ground state and quantifies configurational disorder potentially leading to high-entropy homogeneous single-phases. The methodology is used to seek for disordered refractory 5-metal carbides — potential systems for ultra-high temperature applications. The descriptor correctly predicts a set of candidates that are experimentally synthesized as novel high-entropy homogeneous phases, validating the ansatz of the model. The method has the potential to accelerate the search and development of high-entropy crystalline systems by rationally combining first principles approaches with experimental synthesis.

Author Index

	Wednesday	Thursday	Friday
08:00 - 09:00			**08h40** David Broido 30' p. 44
09:00 - 10:00		**09h00** Olle Hellman 30' p. 27 Johann Bouchet 20' p. 28 Matthew Heine 20' p. 29	Riley Hanus 20' p. 44 Ivana Savic 20' p. 46 Jelena Sjakste 20' p. 47
10:00 - 11:00		Antoine Dewandre 20' p. 30 Coffee	N. Ravichandran 20' p. 48 Coffee
11:00 - 12:00		Alexandre Martin 20' p. 31 Ion Errea 30' p. 32 Raffaello Bianco 20' p. 33	Ambroise van Roekeghem 30' p. 49 Antti Karttunen 20' p. 50 Lucy Whalley 20' p. 51
12:00 - 13:00		Matteo Calandra 20' p. 34 Lunch	Stefano Curtarolo 20' p. 52
13:00 - 14:00	Registration Welcome		
14:00 - 15:00	Atsushi Togo 30' p. 19 Petros Souvatzis 30' p. 20	Olivier Delaire 30' p. 35 Brent Fultz 30' p. 36	
15:00 - 16:00	Chris Marianetti 30' p. 21 Terumasa Tadano 30' p. 22	David Cahill 30' p. 37 Stéphane Pailhes 30' p. 38	
16:00 - 17:00	Coffee Vidvuds Ozolins 30' p. 23	Coffee Xavier Gonze 30' p. 39	
17:00 - 18:00	David Kofke 30' p. 24 Christian Carbogno 30' p. 25	Jarvist Frost 20' p. 40 Vanina Recoules 20' p. 41 Aron Walsh 20' p. 42	
18:00 - 19:00	Albert Glensk 30' p. 26	Brice Arnaud 20' p. 43 Wine cellar	