THEOS

THEORY AND SIMULATION OF MATERIALS

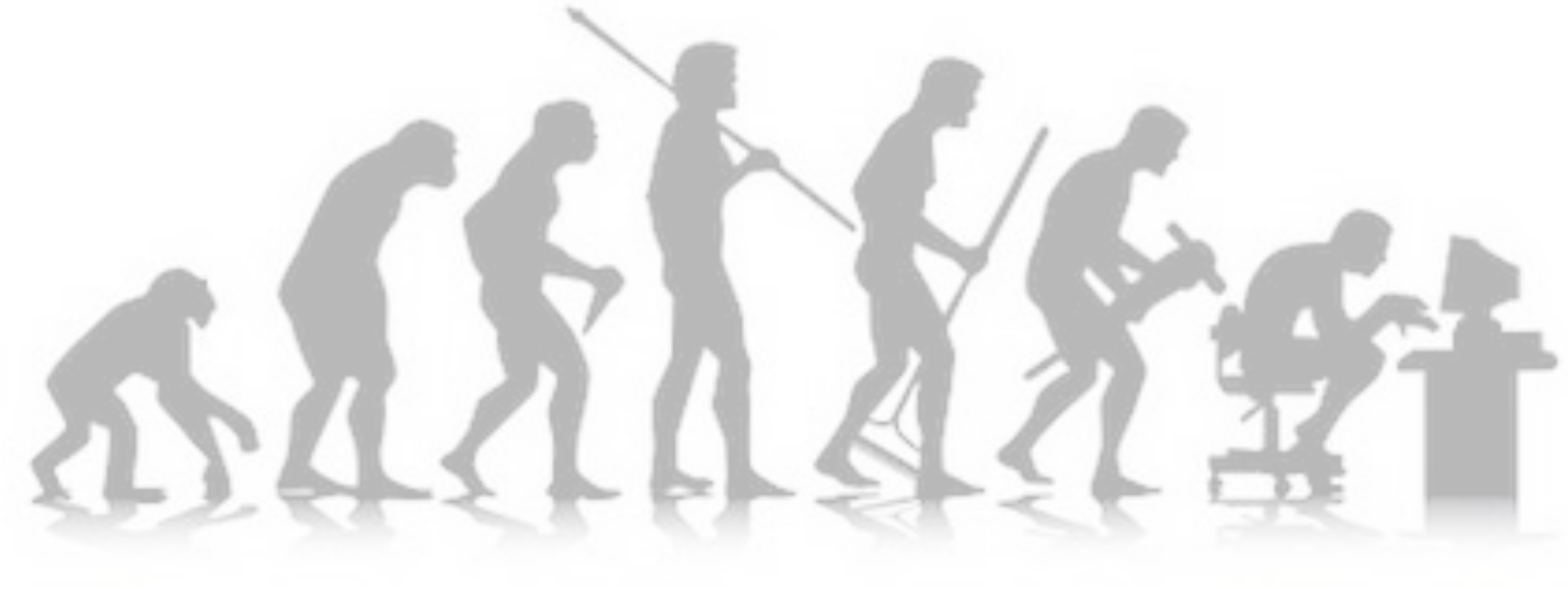
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

AN INDUSTRIAL AGE FOR MATERIALS' SIMULATIONS

Nicola Marzari, EPFL

MATERIALS' ADVANCES ARE KEY TO SOCIETAL WELL BEING

- Human ages are named after materials - stone, bronze, iron, nuclear, silicon…



MATERIALS' ADVANCES ARE KEY TO SOCIETAL WELL BEING

- Human ages are named after materials - stone, bronze, iron, nuclear, silicon…

- We need novel materials for:
  - **Energy and environment:** harvesting, conversion, storage, efficiency
  - **Information and communication technologies:** the entire ICT revolution came from understanding and modelling doped silicon
  - **Fundamental science** emerges from new materials: graphene, quantum computers, high-temperature superconductivity
  - **Experimental science** relies on state-of-the-art materials: detectors, sensors, superconducting magnets
  - **Even pharmaceuticals** are materials: crystallization and polytypes

QUANTUM SIMULATIONS ARE ABLE TO PREDICT MATERIALS' PROPERTIES

2013 Chemistry Prize

Taking the Experiment to Cyberspace

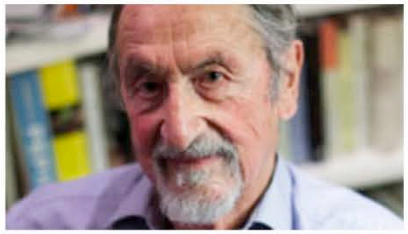


Photo © Harvard University

Martin Karplus

Martin Karplus, U.S. and Austrian citizen. Born 1930 in Vienna, Austria.

Photo: S. Fisch

Michael Levitt

Michael Levitt, U.S., British and Israeli citizen. Born 1947 in Pretoria,

Photo: Wikimedia Commons

Arieh Warshel

Arieh Warshel, U.S. and Israeli citizen. Born 1940 in Kibbutz Sde-

"The prize focuses on how to evaluate the variation in the energy of the real system in a accurate and efficient way […]. **The Car–Parrinello approach is the leading strategy along this line."**

"Simulations are so realistic that they predict the outcome of traditional experiments."

From www.nobelprize.org/nobel_prizes/chemistry/laureates/2013/

AROSA (GRAUBÜNDEN/GRISONS), 27th DECEMBER 1925

At the moment I am struggling with a new atomic theory. I am very optimistic about this thing and expect that if I can only... solve it, it will be very beautiful.

Erwin Schrödinger

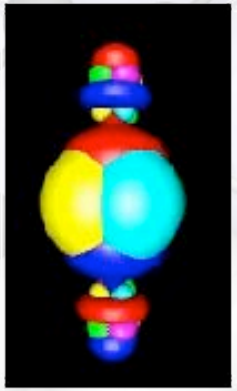
Inhomogeneous Electron Gas
P. Hohenberg and W. Kohn
Phys. Rev. **136**, B864 (9 November 1964)

Self-Consistent Equations Including Exchange and Correlation Effects
W. Kohn and L. J. Sham
Phys. Rev. **140**, A1133 (15 November 1965)

Nobel Focus: Chemistry by Computer

21 October 1998

The 1998 Nobel Prize in chemistry recognizes two researchers whose work has allowed chemists to calculate the properties of molecules and solids on computers, without performing experiments in the lab. The basic principles of the calculation scheme were first described in *Physical Review* in the 1960s, and solid state physicists used them for decades before they became important in the chemistry world. The scheme drastically simplifies the solution of the quantum mechanical equations for a system of many electrons, and although approximate, the solutions are accurate enough that chemists can learn about large molecules without getting their hands wet.



Calculations made easy. Localized orbitals in the electronic structure of the $BaTiO_3$ crystal, calculated using density functional theory, which was invented by 1998 Nobel Laureate Walter Kohn.

Nicola Marzari and David Vanderbilt/Rutgers University

MOST CITED PAPERS IN APS (FROM 1893)

	Journal	# cites	Title	Author(s)
1	PRB (1988)	39190	Development of the Colle-Salvetti Correlation-Energy …	Lee, Yang, Parr
2	PRL (1996)	25452	Generalized Gradient Approximation Made Simple	Perdew, Burke, Ernzerhof
3	PRA (1988)	22904	Density-Functional Exchange-Energy Approximation ...	Becke
4	PR (1965)	20142	Self-Consistent Equations Including Exchange and Correlation …	Kohn and Sham
5	PRB (1996)	13731	Efficient Iterative Schemes for Ab Initio Total-Energy …	Kresse and Furthmuller
6	PRB (1976)	13160	Special Points for Brillouin-Zone Integrations	Monkhorst and Pack
7	PRB (1992)	10876	Accurate and Simple Analytic Representation of the Electron …	Perdew and Wang
8	PRB (1999)	10007	From Ultrasoft Pseudopotentials to the Projector Augmented …	Kresse and Joubert
9	PRB (1990)	9840	Soft Self-Consistent Pseudopotentials in a Generalized …	Vanderbilt
10	PR (1964)	9789	Inhomogeneous Electron Gas	Hohenberg and Kohn
11	PRB (1981)	9787	Self-Interaction Correction to Density-Functional Approx. …	Perdew and Zunger
12	PRB (1992)	9786	Atoms, Molecules, Solids, and Surfaces - Applications of the …	Perdew, Chevary, …
13	PRB (1986)	9313	Density-Functional Approx. for the Correlation-Energy …	Perdew
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15	PRB (1994)	9100	Projector Augmented-Wave Method	Blochl
16	PRL (1980)	7751	Ground-State of the Electron-Gas by a Stochastic Method	Ceperley and Alder
17	PRL (1987)	7663	Inhibited Spontaneous Emission in Solid-State Physics …	Yablonovitch
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22	PR (1957)	6260	Theory of Superconductivity	Bardeen, Cooper, Schrieffer

N. Marzari, Feb 2013

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N. Marzari, Feb 2013

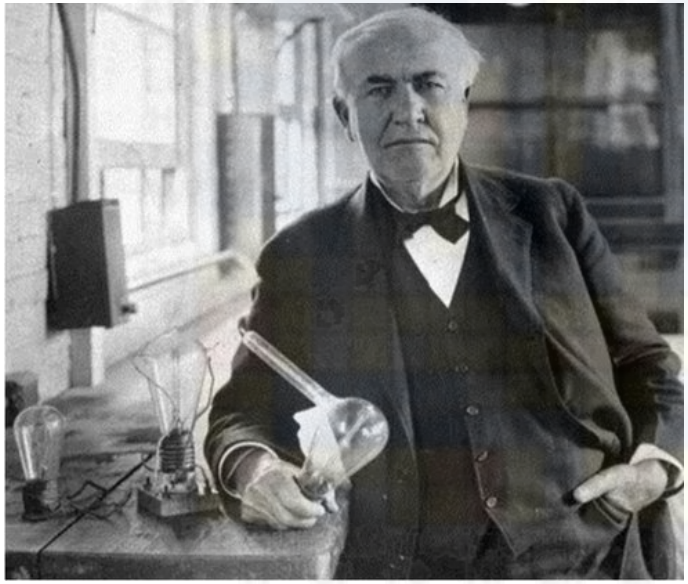
PAPERS PUBLISHED IN 2013 USING QUANTUM SIMULATIONS CODES

- **VASP** **~2700**
- **Quantum-ESPRESSO** **~800**
- **SIESTA** **~590**
- **CASTEP** **~410**
- **NWCHEM** **~230**
- **Abinit** **~130**

+ CPMD, CP2K (no reference count)

MATERIALS' DEVELOPMENT STILL EDISONIAN: INTUITION, SEARCHES, AND SERENDIPITY

- Edison tested 3000 materials for his filament – settling on burned sewing thread.



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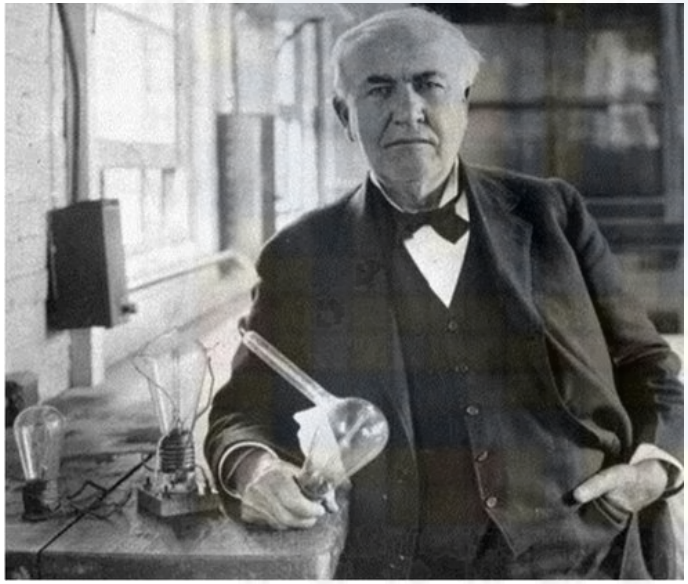
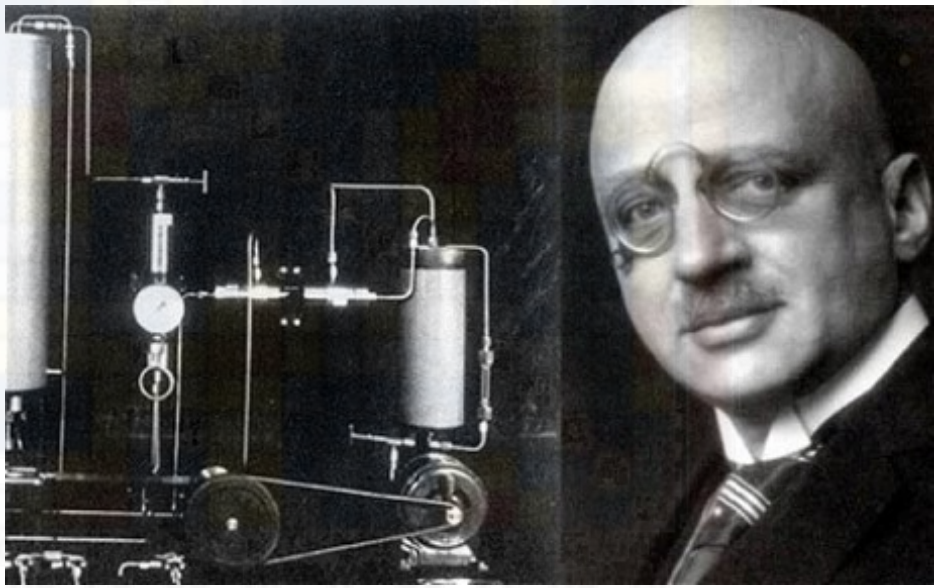
- Haber–Bosch ammonia synthesis used osmium as catalyst. Mittasch (BASF) tested more than 22,000 materials to identify the iron-based catalyst which is still used today.





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- Norskov showed in 2009 that CoMo is a more efficient inexpensive catalyst.

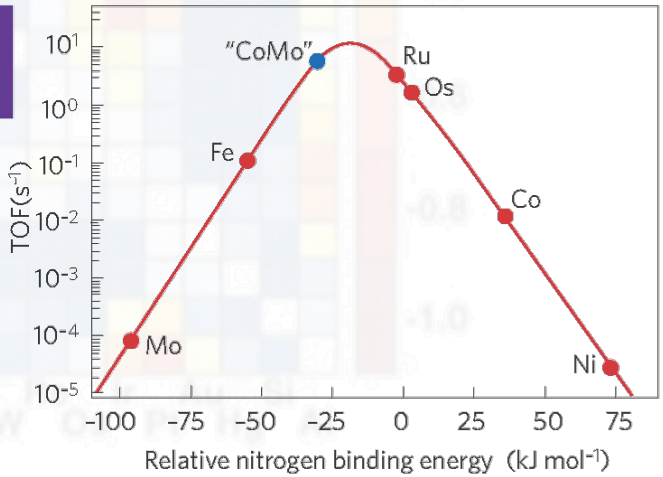
nature chemistry

REVIEW ARTICLE

PUBLISHED ONLINE: 19 MARCH 2009 | DOI: 10.1038/NCHEM.121

Towards the computational design of solid catalysts

J. K. Nørskov[1]*, T. Bligaard[1], J. Rossmeisl[1] and C. H. Christensen[2]



COMPUTATIONAL MATERIALS' DESIGN

TUNNELLING MAGNETORESISTANCE (TMR):

- 2001: giant TMR predicted in crystalline barrier oxides (Fe|MgO|Fe junctions): **T. Schulthess et al**, Phys. Rev. B 63, 54416 (2001)
- 2004: single crystal giant-TMR junctions realized in experiments: Nature Materials 3, 862 (2004), Nature Materials 3, 868 (2004)
- 2007: commercial large-capacity hard-disks
- 2008: 98.4% of the 530 million hard disk shipped

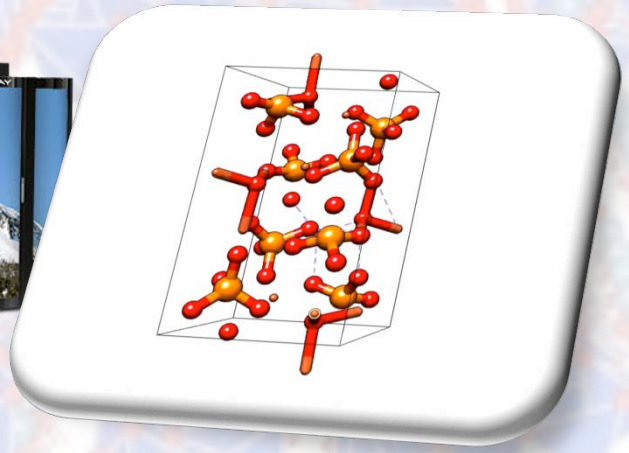
HIGH-K MATERIALS FOR GATE OXIDES IN CMOS:

- 2004-07: Theoretical predictions by **A. Curioni et al.**, Phys. Rev. Lett. 92, 236405 (2004), ibid. 94, 146401 (2005), ibid. 98, 037602 (2007)
- 2006-12: Patents "Methods of forming metal/high-K gate stacks with high mobility" (US 7115959 and US8153514)
- Technology used today in all the IBM high-end platforms and in most of Apple and Samsung smartphones and tablets

THROUGHPUT CAPACITY DOUBLES EVERY 14 MONTHS

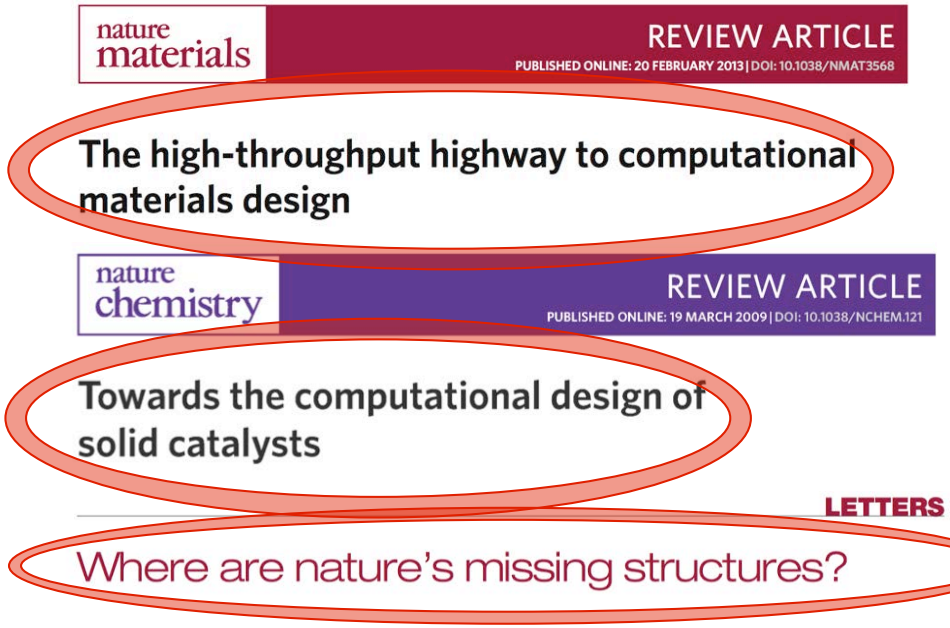
The number of inorganic materials known in full (i.e. with published structures) is **150,000**

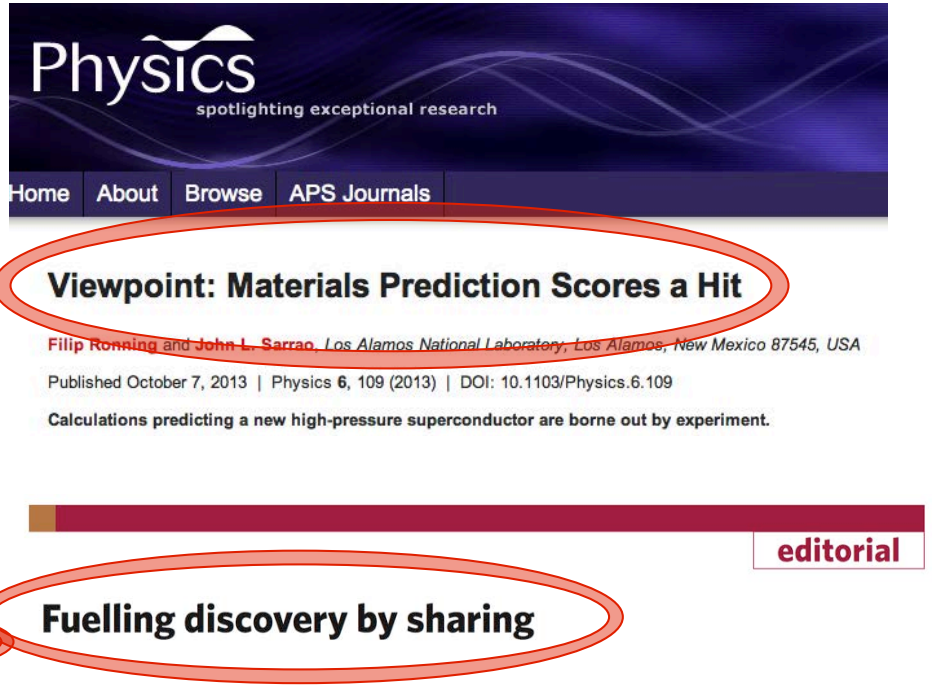
Currently, very basic properties can be calculated on the entire current Swiss supercomputer (Piz Daint, #6 in the world) at the tune **of 500 structures/minute**. In 12 years: **500,000/minute**



QUANTUM SIMULATIONS OF MATERIALS: TIMELY, NEEDED, AND TRANSFORMATIONAL

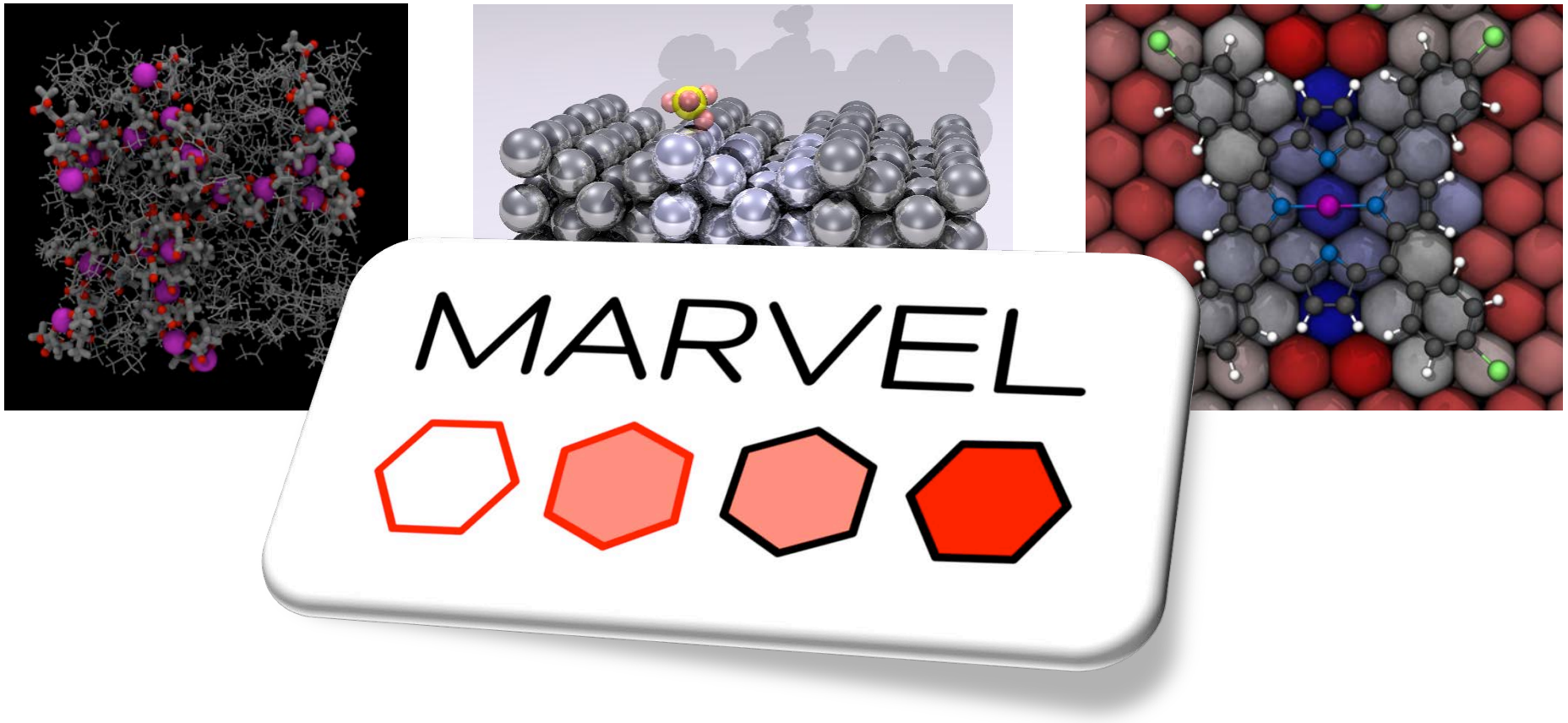
Quantum simulations are unique in their power to accelerate discovery, with **societal advances and well-being relying critically on novel materials**





SWISS NATIONAL CENTER @ EPFL

MATERIALS' REVOLUTION: COMPUTATIONAL DESIGN AND DISCOVERY OF NOVEL MATERIALS



12 YEAR EFFORT (2014-26), 20+ PIs

EPFL (Marzari, Pasquarello, Roethlisberger, Koch, Andreoni, Corminboeuf, Yazyev, Ceriotti), ETHZ (Spaldin, Troyer, VandeVondele), Basel (Goedecker, Von Lilienfeld), Fribourg (Werner), Geneva (Georges), Svizzera Italiana (Parrinello), Zurich (Hutter), IBM (Curioni), CSCS (Schulthess), EMPA (Groning, Passerone), PSI (Kenzelman, Nolting)

STRUCTURAL PLANS

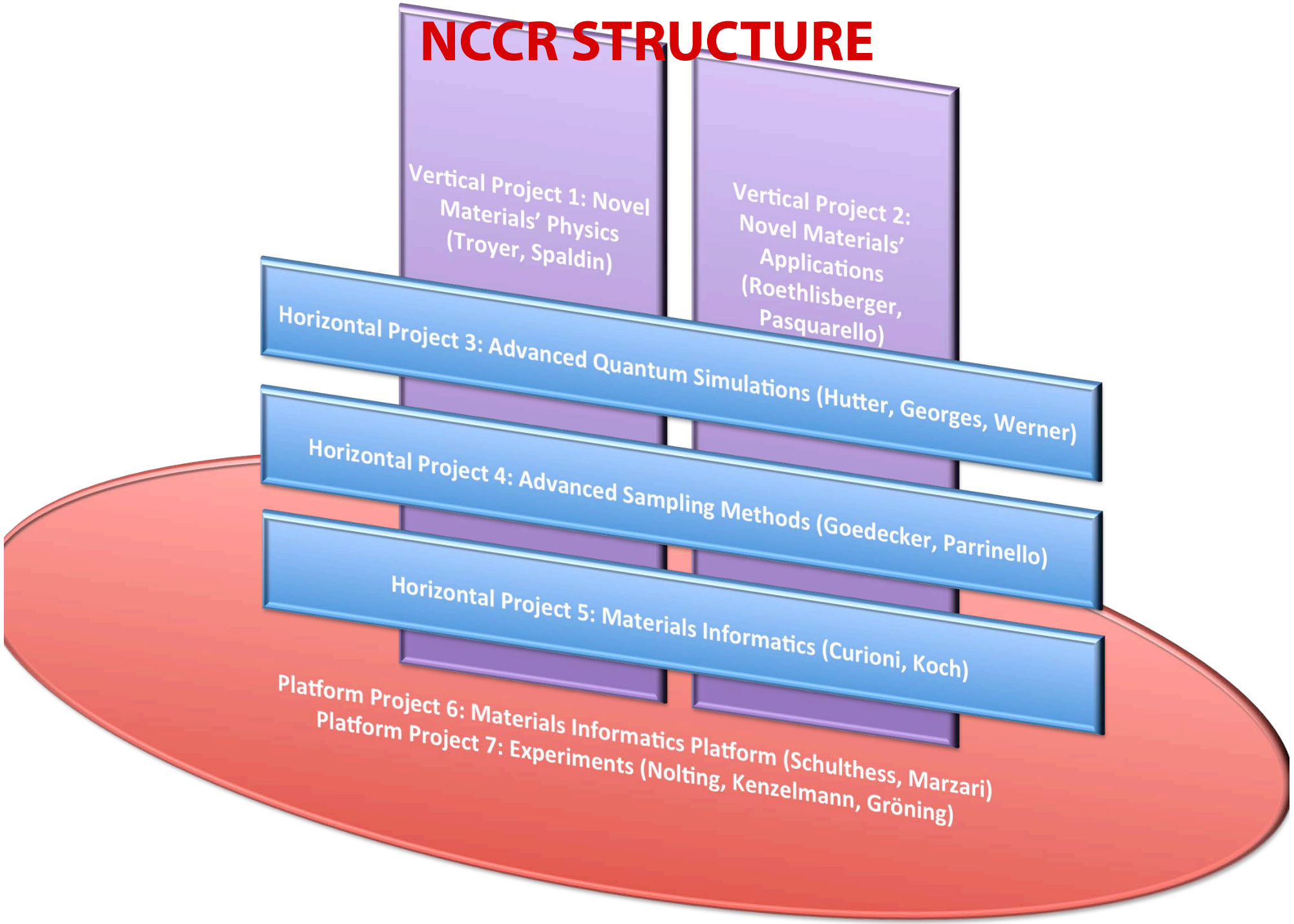
1st Phase (2014-18) funded with 27M CHF (18M from SNSF and 9M from EPFL), includind 3 tenure-track chairs

- Computational physics
- Computational materials science
- Data mining and machine learning

Also happening at EPFL

- **2 full professor hires in 2013 for scientific computation, energy**
  - **Prof Jan Hesthaven** (from Brown U.): new Chair of Computational Mathematics and Simulation Science
  - **Prof Berend Smit** (from UC Berkeley, Director of DOE Energy Research center): world expert in molecular modelling for energy
- **CECAM** (Centre Européen de Calcul Atomique et Moléculaire) moved to EPFL (45-year history; 20 workshops/year @ EPFL/ETHZ/USI)

NCCR STRUCTURE



HP5: INTERSECTION OF FUNDAMENTAL SCIENCE, COMPUTER SCIENCE, AND BIG DATA

- Integrate and leverage the concepts and tools of computer science with computational modelling:
  - **machine learning and cognitive computing**
  - **data mining, graph analytics and "big data"**

- Revolutionize and democratize science by making it shared by many "in the cloud"

- Make computational experiments database-driven, database-filling

WHAT DO WE NEED?

1 ACCURACY (VERIFICATION AND VALIDATION)

2 COMPLEXITY (MACRO FROM MICRO)

3 REPRODUCIBILITY AND SYSTEMATICITY

PHYSICAL REVIEW B **79**, 174107 (2009)

Ground state structure of $BaZrO_3$: A comparative first-principles study

Ante Bilić*
Materials Theory and Simulation Laboratory, Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis 138632, Singapore

Julian D. Gale
Department of Applied Chemistry, Nanochemistry Research Institute, Curtin University of Technology, P.O. Box U1987, Perth 6845, Western Australia

(Received 10 February 2009; published 7 May 2009)

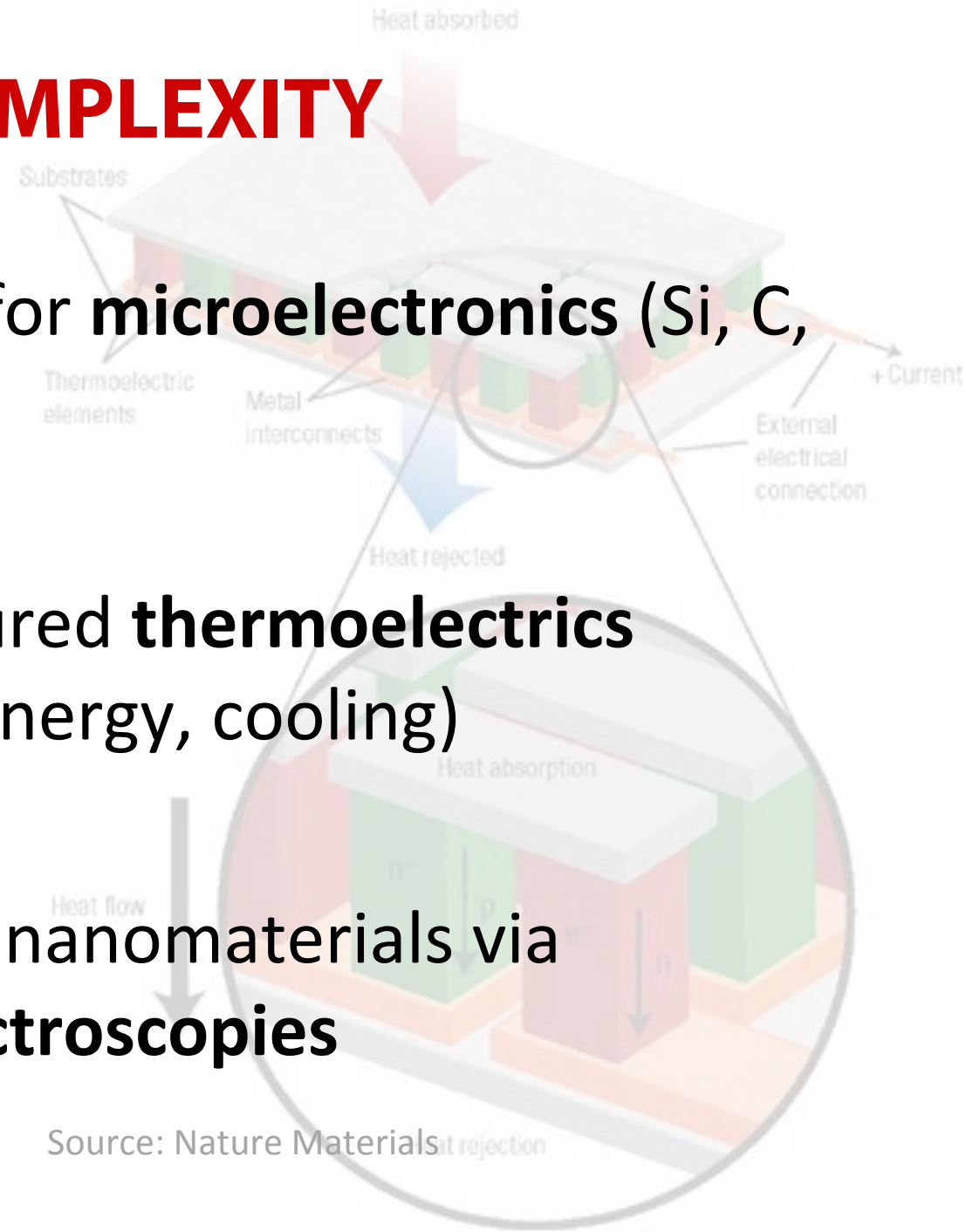
First-principles calculations, based on density-functional theory, are exploited to investigate the nature of the ground-state structure of barium zirconate. The experimentally observed simple-cubic structure is found to be dynamically unstable against an antiferrodistortive transformation. This instability manifests itself through imaginary frequency modes along the whole R-M edge of the Brillouin zone. The computations predict an orthorhombic crystal structure [illegible], only slightly distorted from the cubic lattice, with an eight times larger unit cell and alternate ZrO_6 octahedra slightly rotated in opposite directions around the Cartesian axes. The apparent disagreement with some of the previous first-principles results regarding the nature of the ground-state structure is considered in detail. The neglect of the barium $5s^2$ and $5p^6$ electrons in the valence configuration of Ba is found to be responsible for the previously reported erroneous results.

VERIFICATION

Thus, the appropriateness of the present XXX potentials for the structural and dynamical investigations of perovskites is, at best, dubious and users should be encouraged to generate more transferable pseudopotentials.

COMPLEXITY

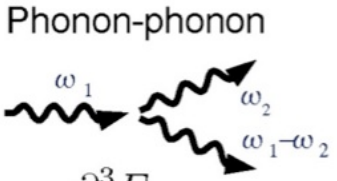
- Nanoscale devices for **microelectronics** (Si, C, MX_2 , molecular…)
- Bulk or nanostructured **thermoelectrics** (harvesting waste energy, cooling)
- Characterization of nanomaterials via **first-principles spectroscopies**



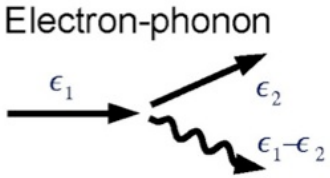
Source: Nature Materials

Approach I: Semiclassical

1. Vibrational properties from density-functional theory (electrons from many-body perturbation theory)
2. Carriers' scattering rates from density-functional perturbation theory (www.quantum-espresso.org)



$$\frac{\partial^3 E}{\partial u_1 \partial u_2 \partial u_3}$$

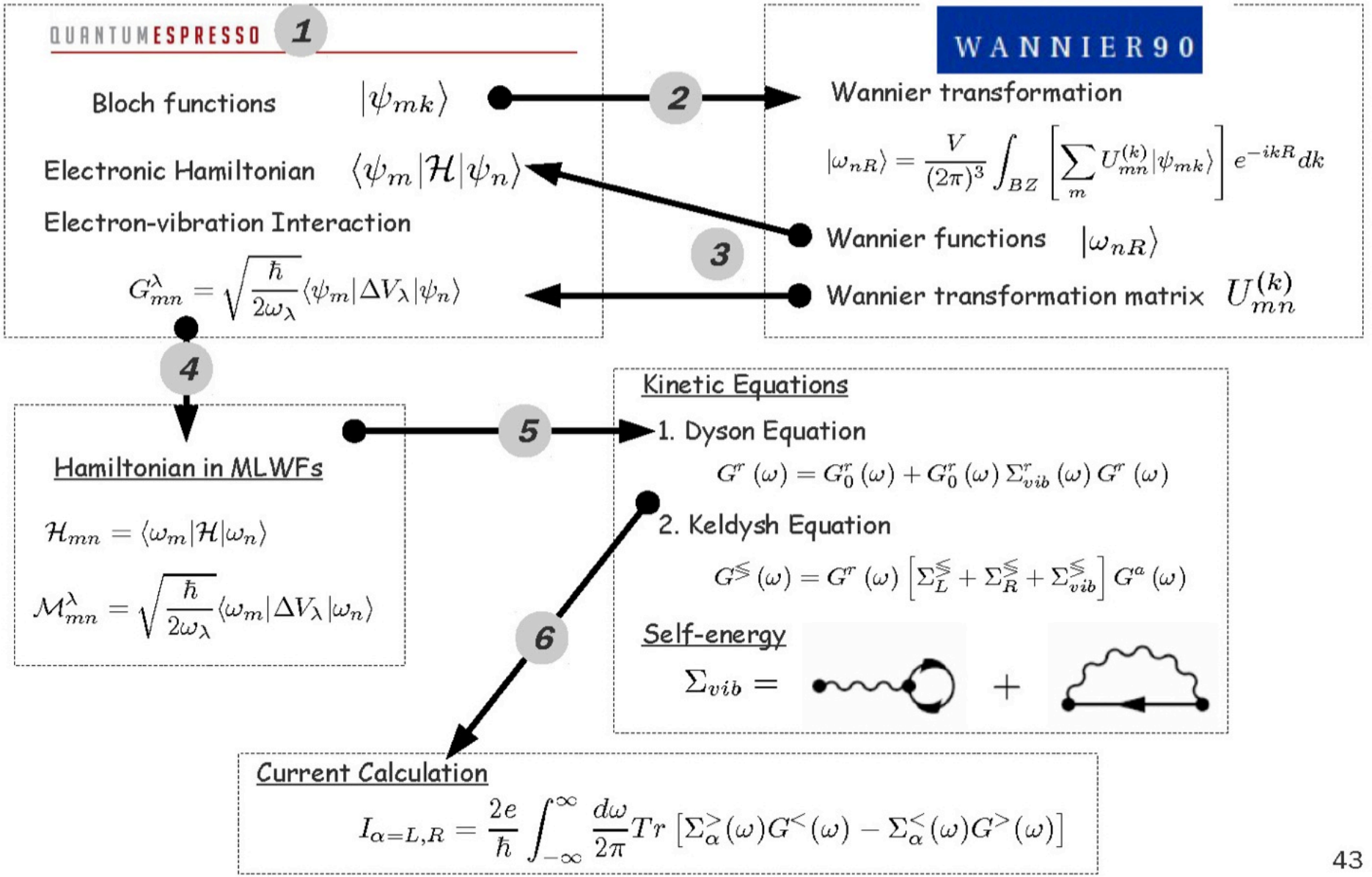


$$\langle \mathbf{k}+\mathbf{q}, j \mid \Delta V_{\mathbf{q},\lambda} \mid \mathbf{k}, i \rangle$$

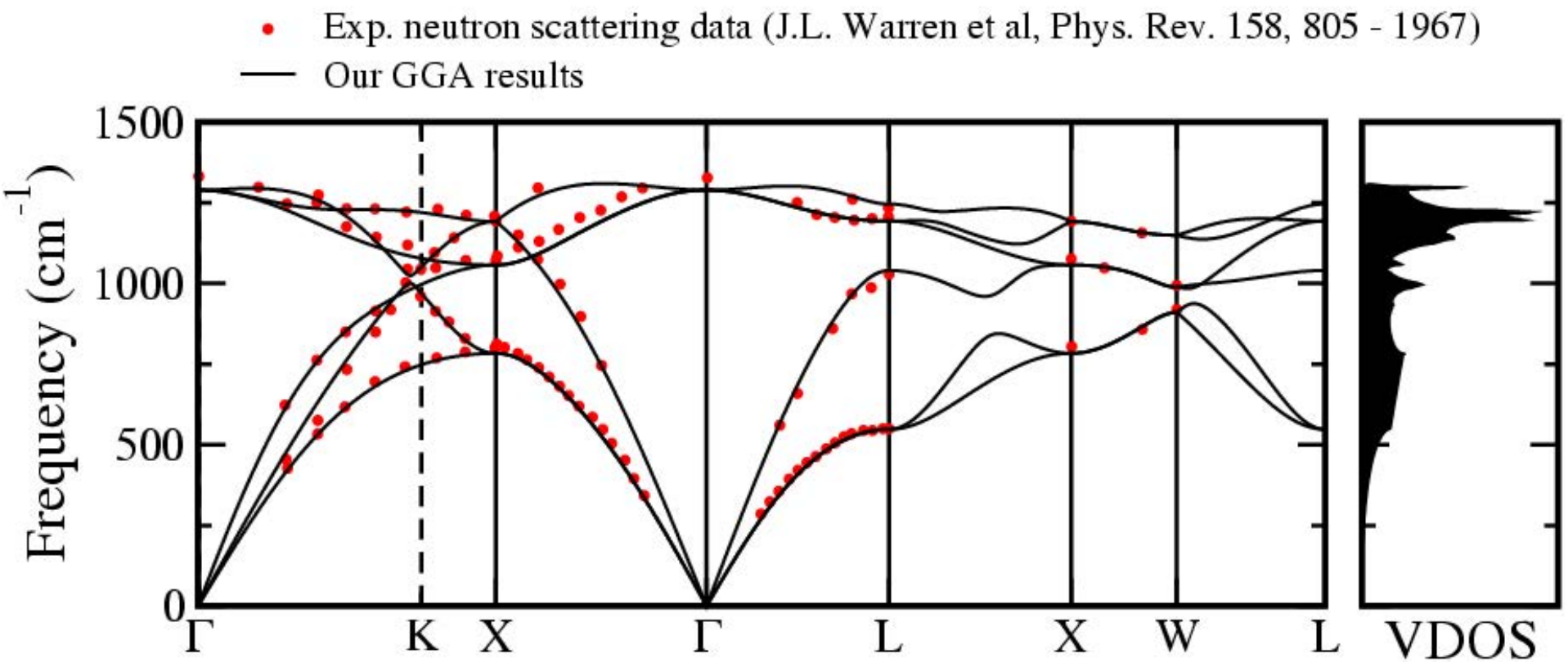
3. Wannier interpolations (www.wannier.org, epw.org.ac.uk)
4. Transport properties from Boltzmann's equation

$$\begin{cases} \left.\frac{\partial n_\lambda}{\partial t}\right|_{scatt} = \frac{\partial \omega_\lambda}{\partial \mathbf{q}} \cdot \nabla T \left(\frac{\partial n_\lambda}{\partial T}\right) & \text{(phonons)} \\ \left.\frac{\partial f_\mu}{\partial t}\right|_{scatt} = \frac{1}{\hbar}\frac{\partial \epsilon_\mu}{\partial \mathbf{k}} \cdot \nabla T \left(\frac{\partial f_\mu}{\partial T}\right) + \frac{e}{\hbar}\mathbf{E} \cdot \frac{\partial f_\mu}{\partial \mathbf{k}} & \text{(electrons)} \end{cases}$$

Approach II: Quantum

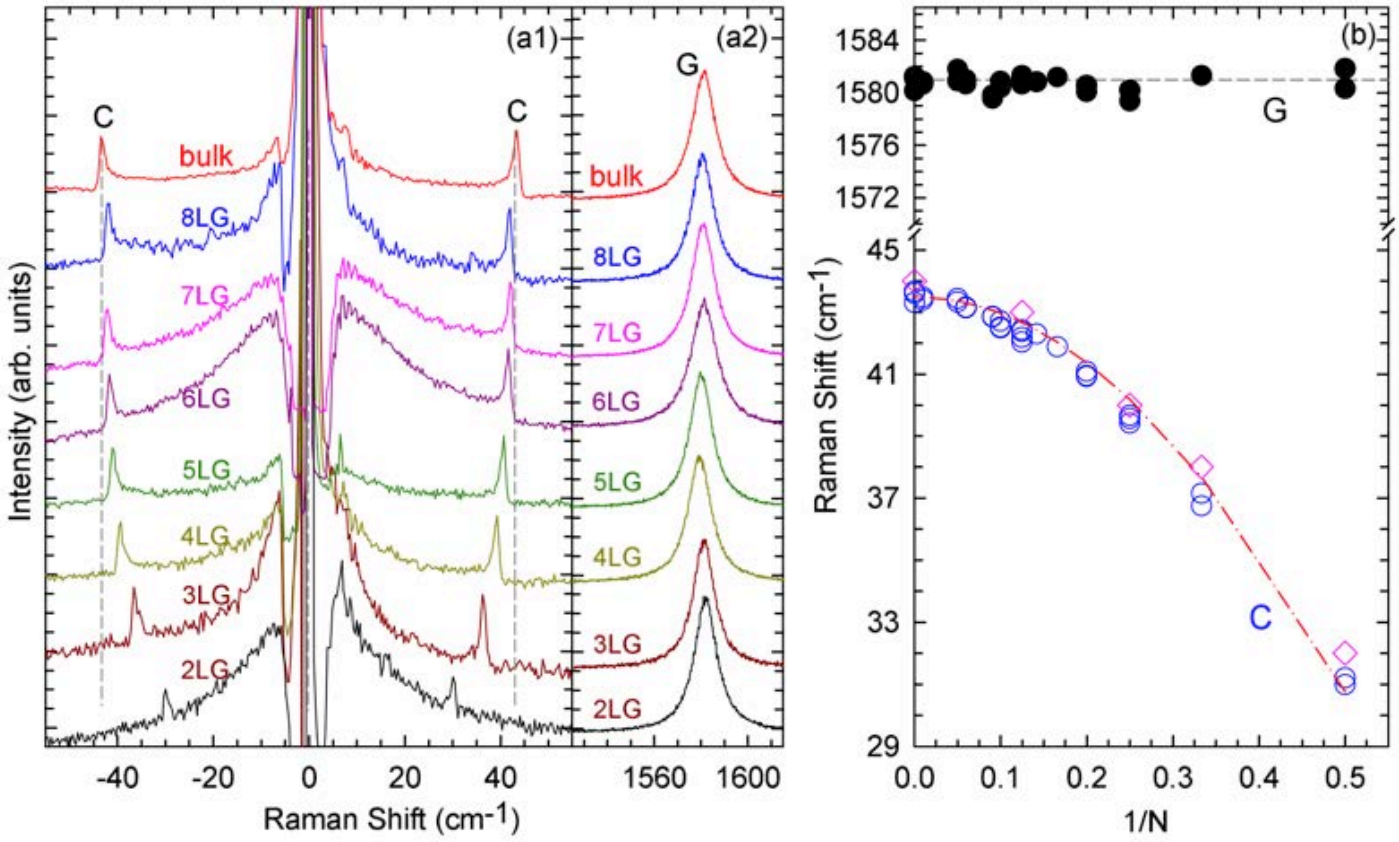


Diamond (on a cell phone; Nokia N900)



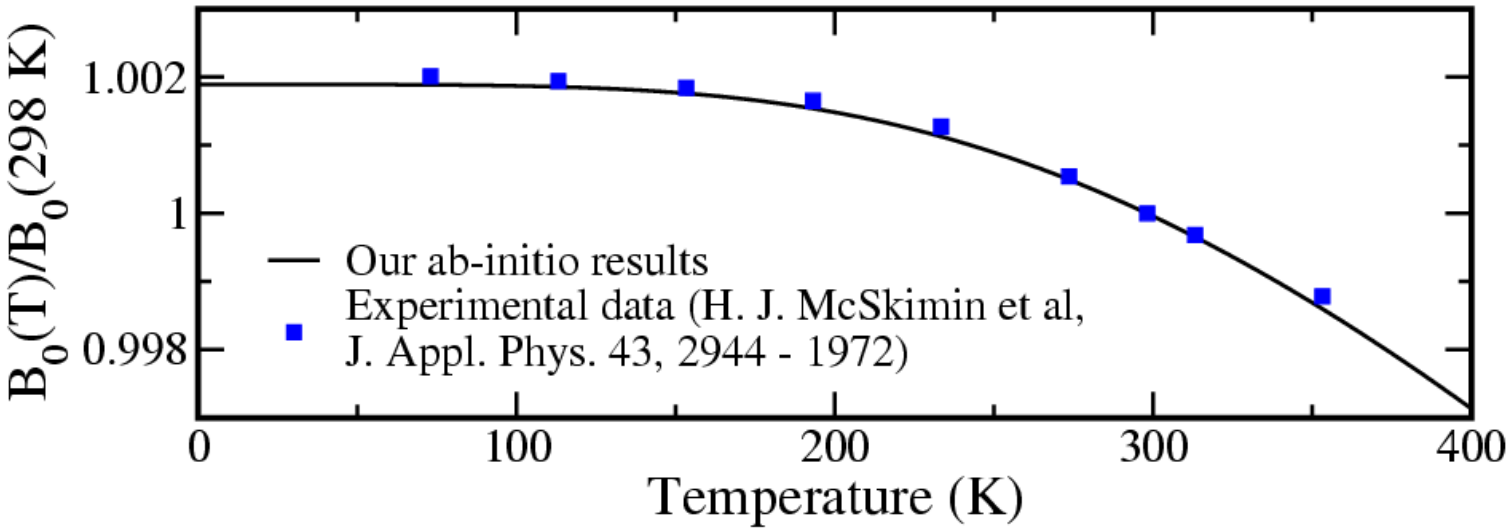
N. Mounet and N. Marzari, Phys. Rev. B (2005)

Multilayer graphene

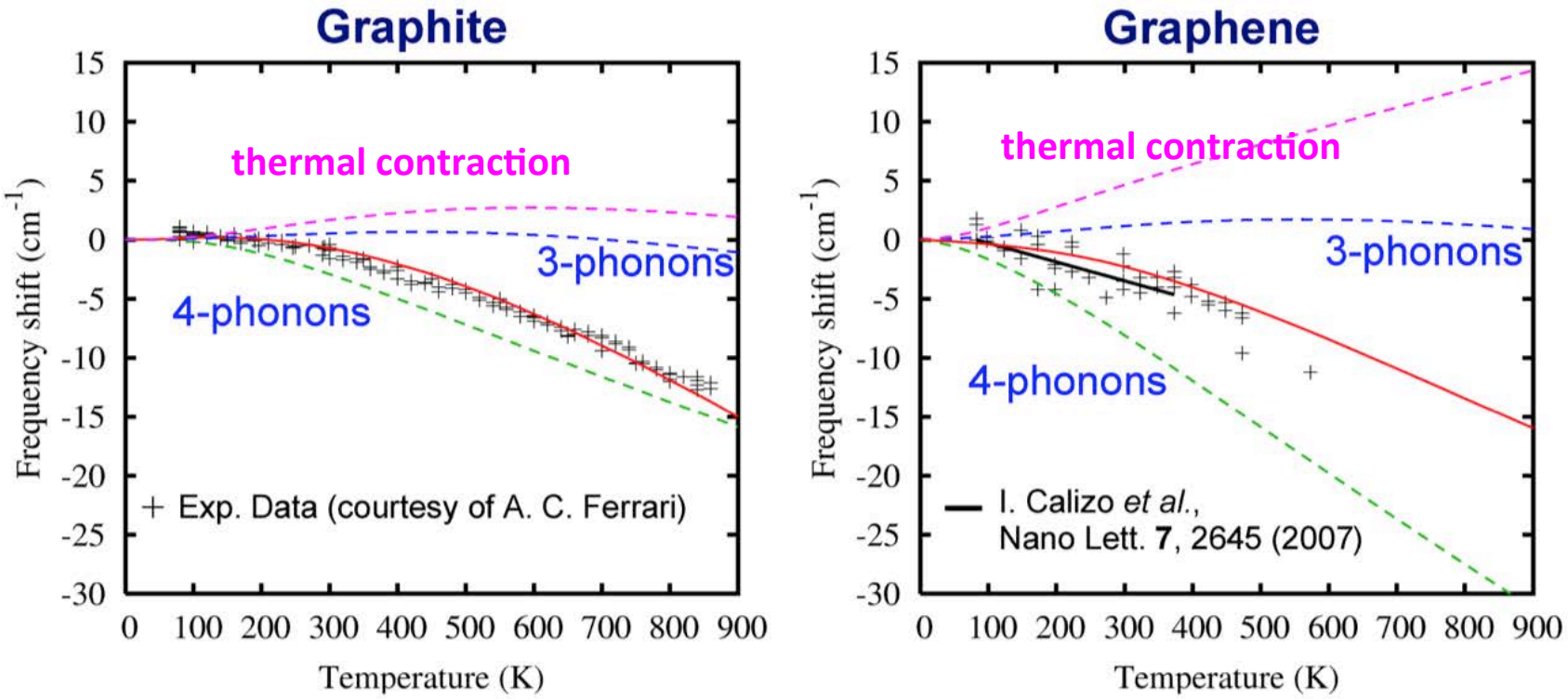


Nature Materials 2012, with AC Ferrari (U. of Cambridge)

Thermomechanics (bulk modulus of diamond)

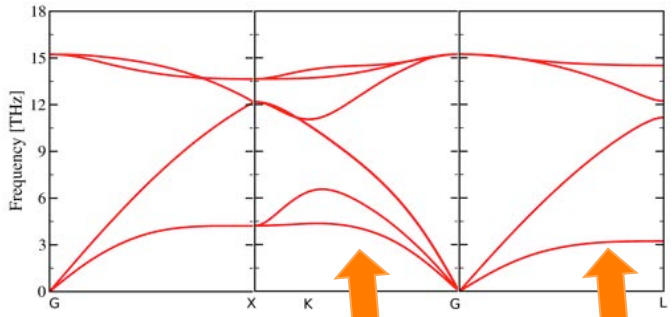


Validation through spectroscopies

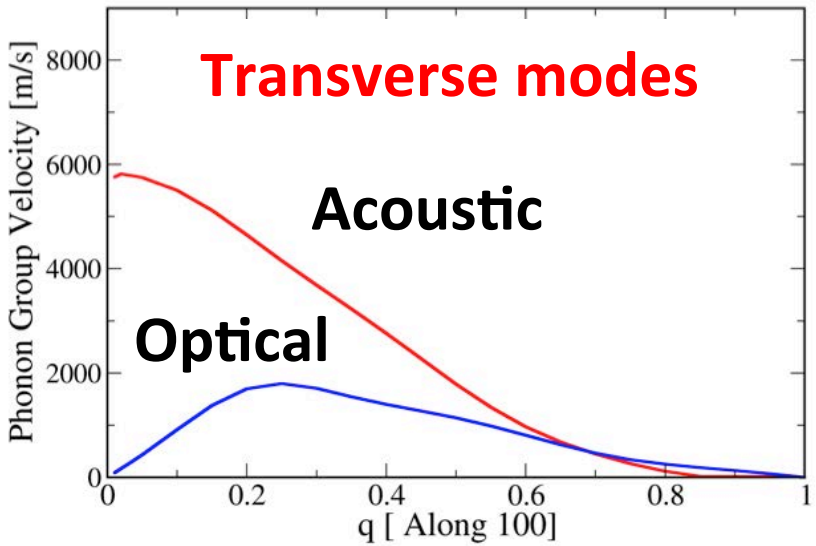


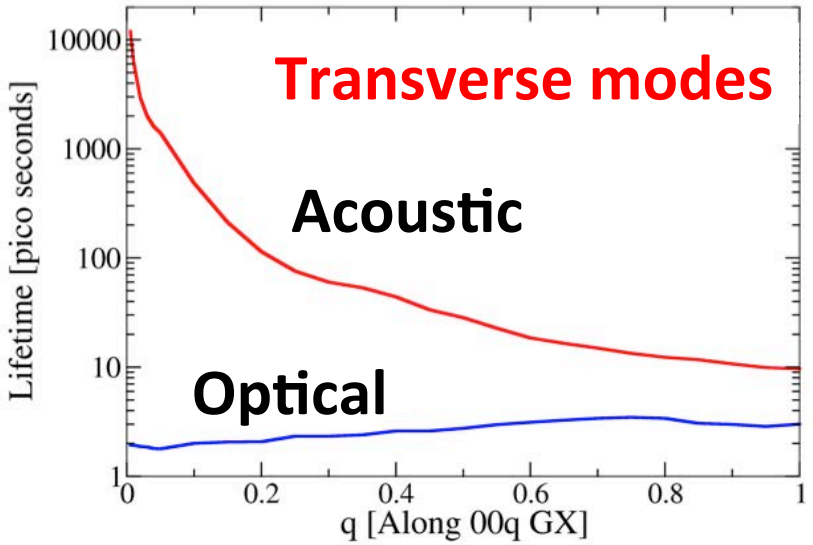
N. Bonini *et al.*, Phys. Rev. Lett. 99 176802 (2007)

Thermal conductivity

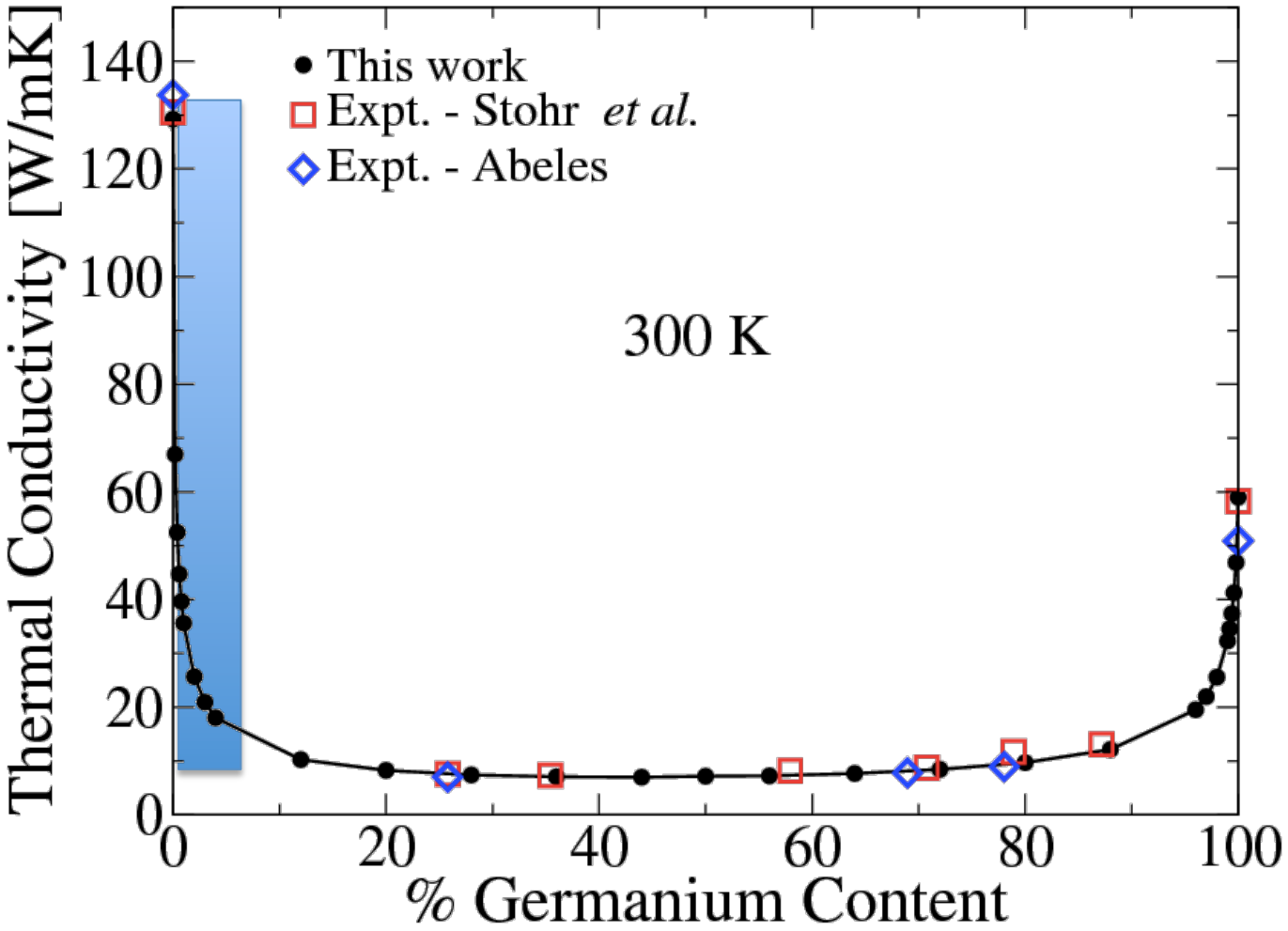


$$K = \frac{\hbar^2}{3N_0\,\Omega k_B T^2} \sum_{qs} c_s^2(q)\,\omega^2(qs)\,\bar{n}_{qs}\,(\bar{n}_{qs}+1)\,\tau_{qs}$$



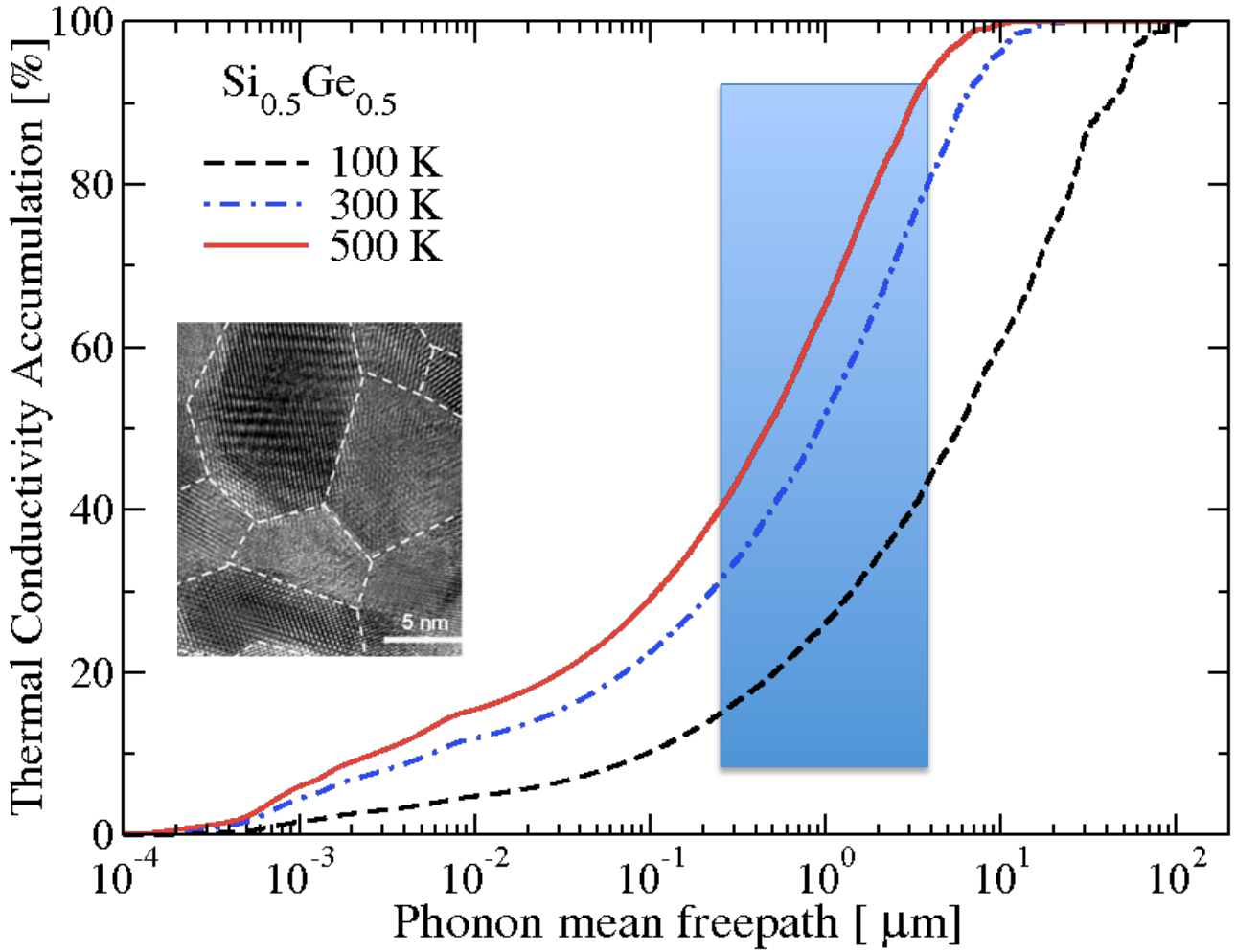


Composition dependence in SiGe alloys



J. Garg, N. Bonini, B. Kozinsky and N. Marzari, Phys. Rev. Lett. (2011)

Mean free paths in SiGe alloys



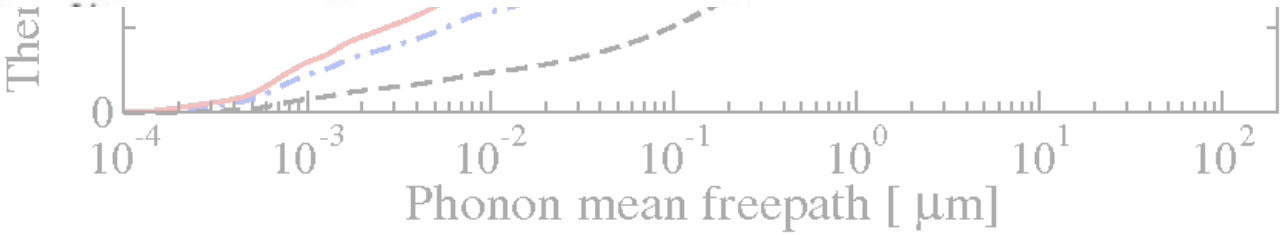
J. Garg, N. Bonini, B. Kozinsky and N. Marzari, Phys. Rev. Lett. (2011)

Mean free paths in SiGe alloys

ARTICLES
PUBLISHED ONLINE: 30 JUNE 2013 | DOI: 10.1038/NNANO.2013.121
nature nanotechnology

Observation of room-temperature ballistic thermal conduction persisting over 8.3 μm in SiGe nanowires

Tzu-Kan Hsiao[1,2], Hsu-Kai Chang[3], Sz-Chian Liou[1], Ming-Wen Chu[1], Si-Chen Lee[3] and



J. Garg, N. Bonini, B. Kozinsky and N. Marzari, Phys. Rev. Lett. (2011)

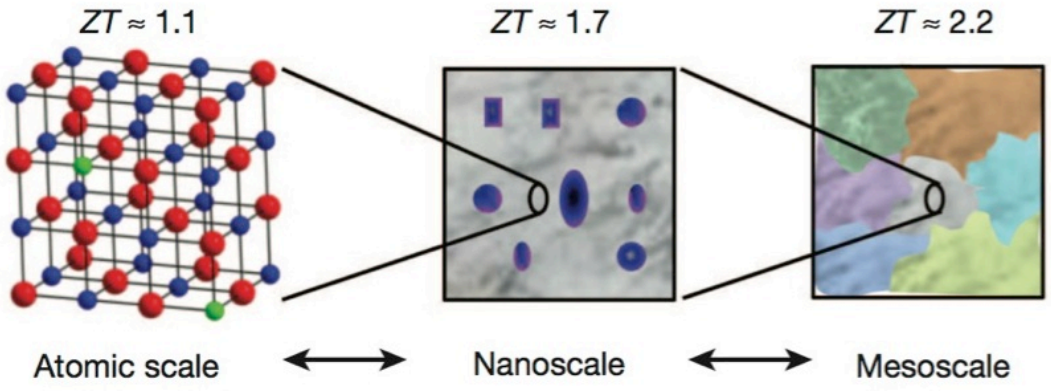
Engineering high-performance thermoelectrics

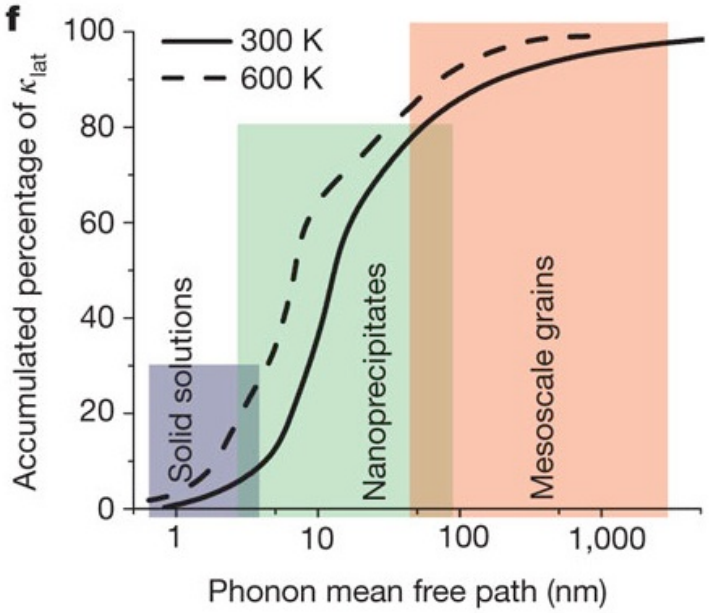
LETTER

doi:10.1038/nature11439

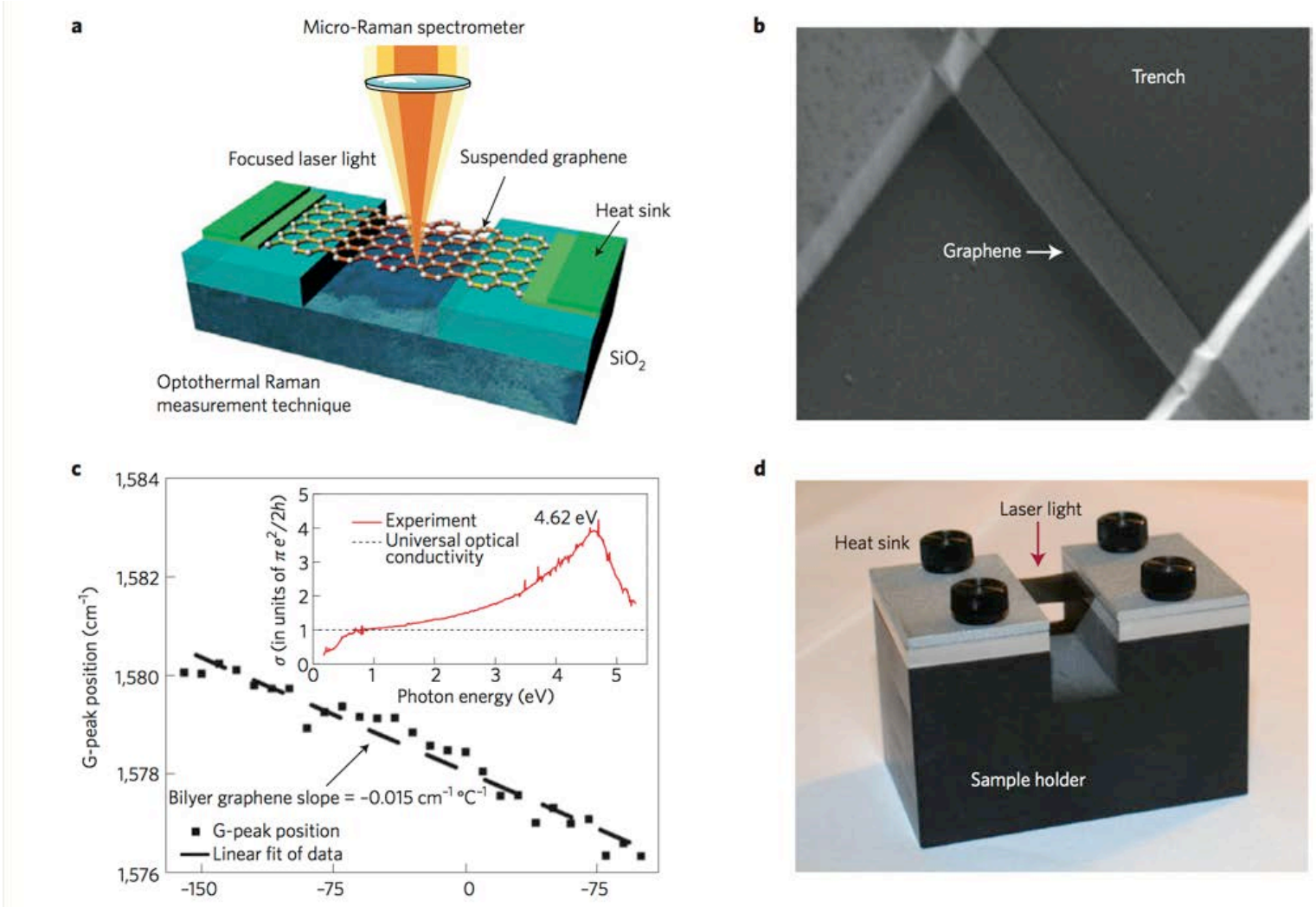
High-performance bulk thermoelectrics with all-scale hierarchical architectures

Kanishka Biswas[1]†, Jiaqing He[1,2]†, Ivan D. Blum[2], Chun-I Wu[3], Timothy P. Hogan[3], David N. Seidman[2], Vinayak P. Dravid[2] & Mercouri G. Kanatzidis[1,4]



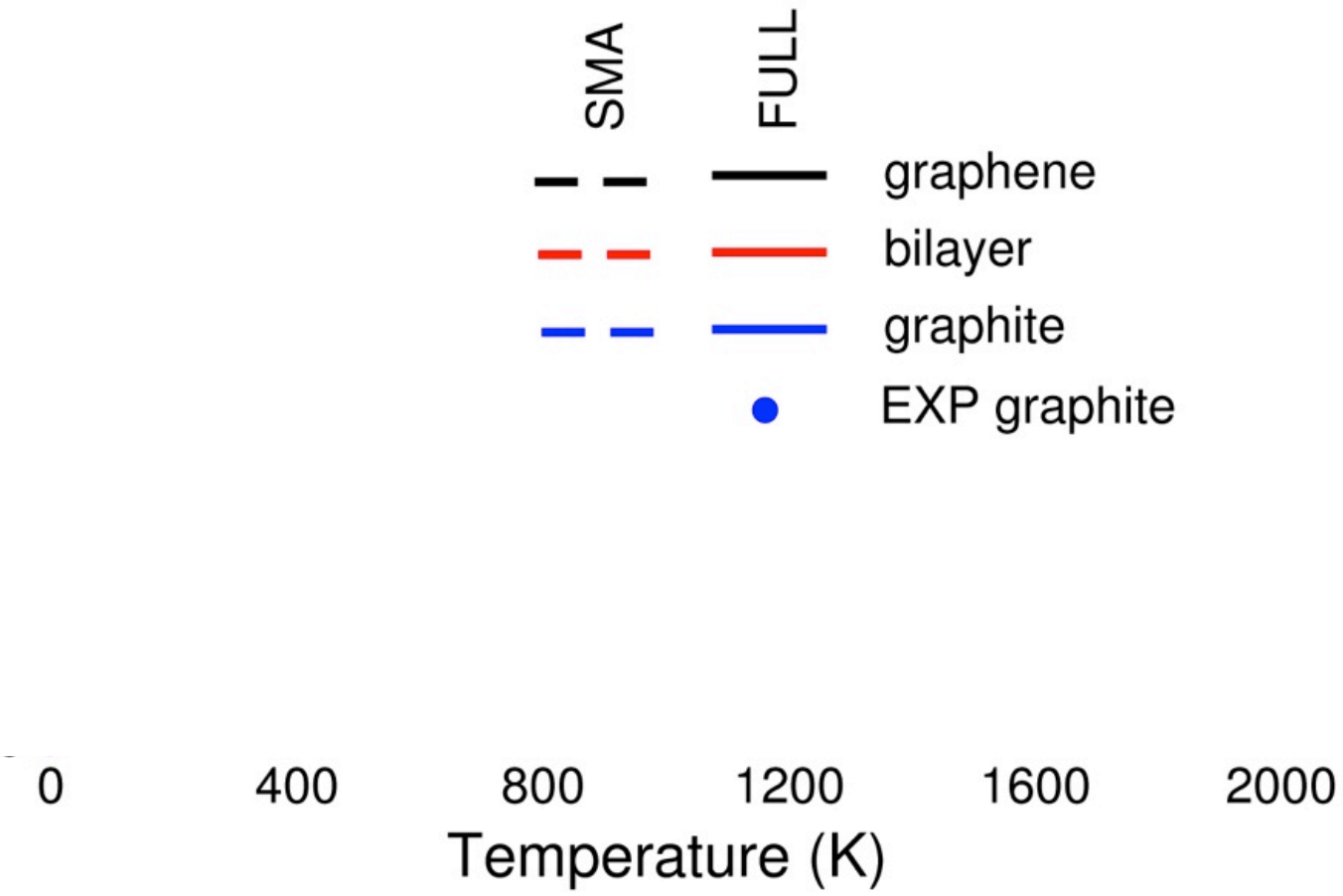


What about 2D materials?



A. Balandin, Nature Materials (2011)

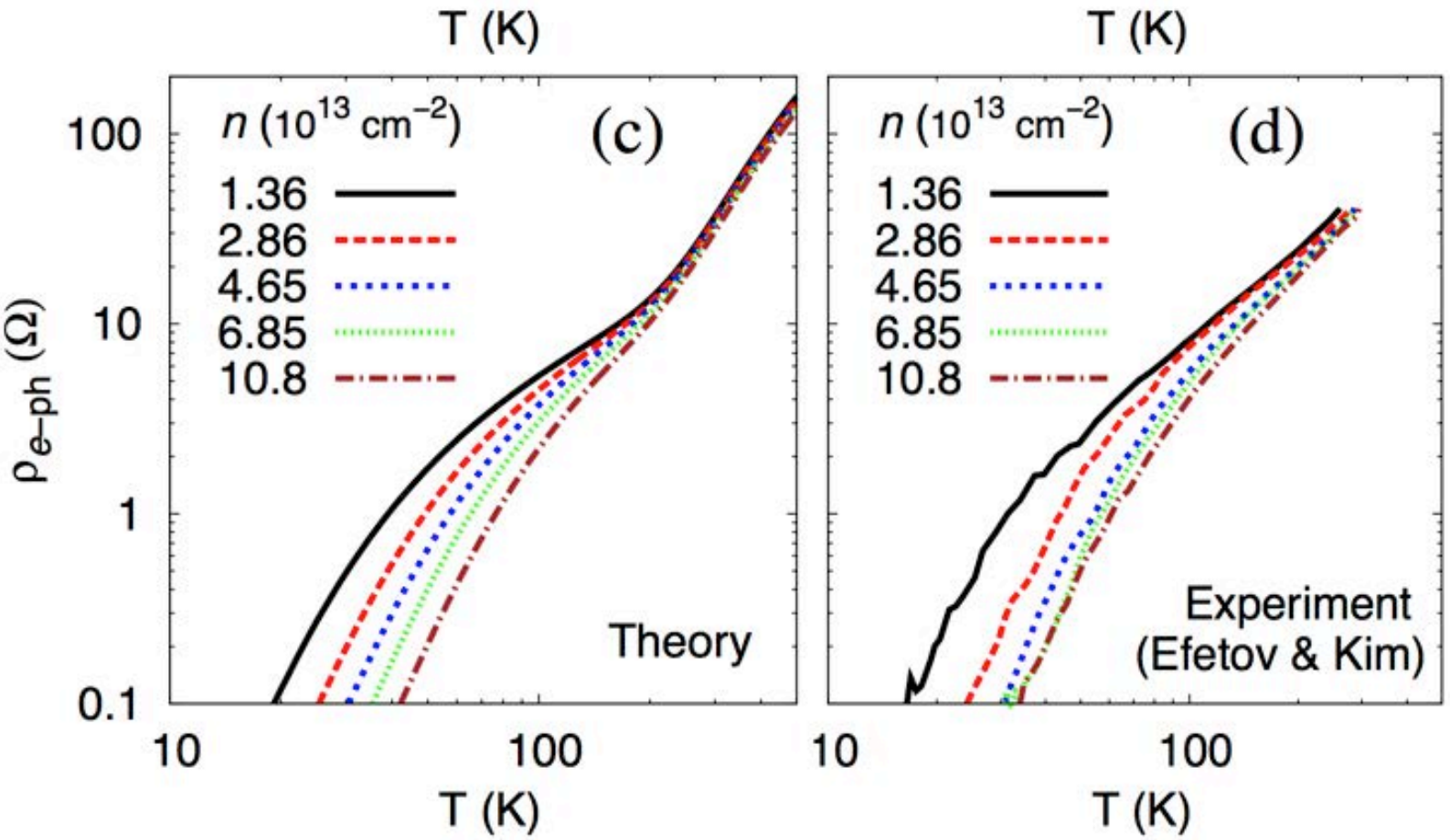
In-plane: Graphite, bilayer, monolayer



Thermal conductivity of graphene

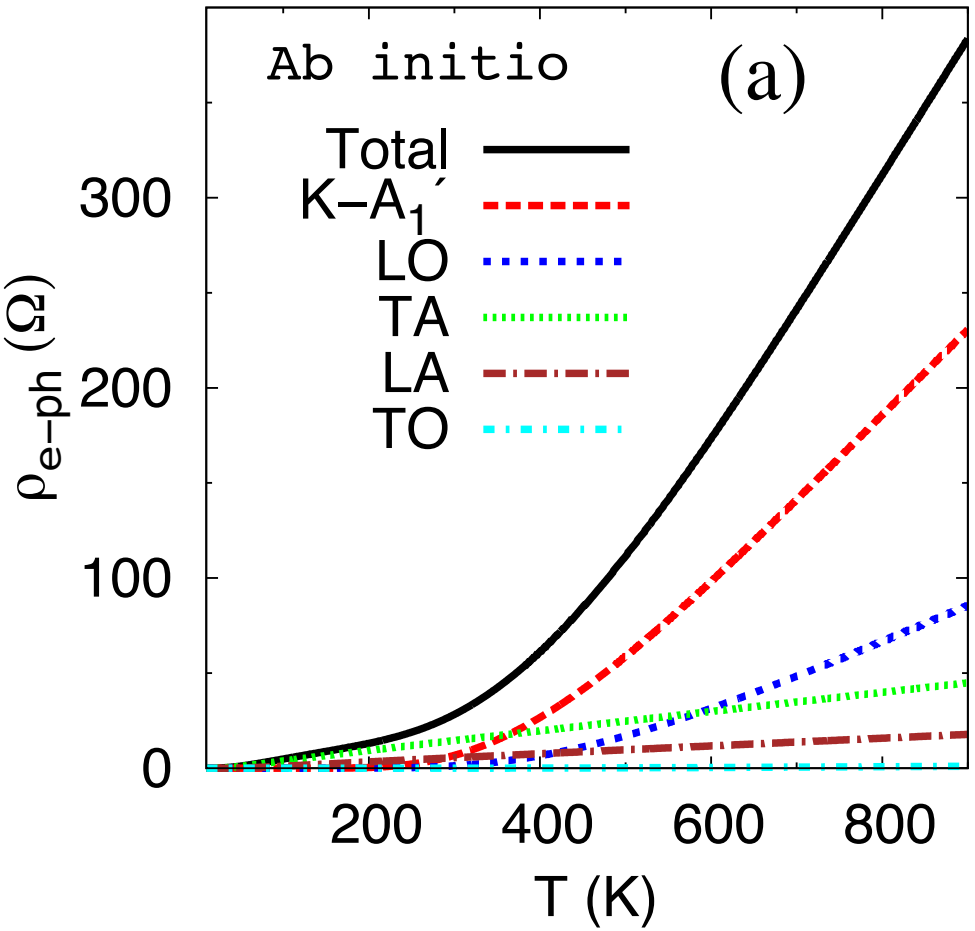
Expts: A. Balandin, Nature Materials (2011)

Electrical resistivity from el-ph scattering: graphene (T, doping)



Cheol Hwan Park, Nicola Bonini, et al., Nano Letters (2014)

Electrical resistivity in graphene



Cheol Hwan Park, Nicola Bonini, et al., Nano Letters (2014)

RUN COMPUTER LABORATORIES WITH A MATERIALS' INFORMATIC PLATFORM: PREPARE, ORGANIZE, RUN, COMBINE, REPEAT, STORE, DATAMINE, SHARE…

an automation tool

automatic job submission, retrieval and parsing

a library

database of structures, pseudopotentials, jobs, job results...

a librarian

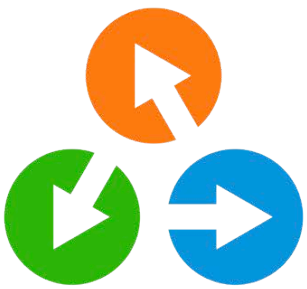
job tracking and organization of all present and future activities of a group

a network of libraries

possibility to share the database (or portions of it) with other groups

AUTOMATED INTERACTIVE INFRASTRUCTURE AND DATABASE FOR ATOMISTIC SIMULATIONS

GIOVANNI PIZZI, ANDREA CEPELLOTTI, RICCARDO SABATINI, NM @ EPFL
BORIS KOZINSKY @ ROBERT BOSCH (CAMBRIDGE MA)



AiiDA

Automatization

Reduce human time spent performing routine operations (file copy, submission and retrieval, ...)

Hybrid database

Sql-NoSql hybrid database implemented within an Sql backend

- Flexible structure
- Fast querying

Plugin interface

All components written with a plugin interface

Virtually any code, cluster and scheduler are supported

Sharing

Data is private, but easily shareable

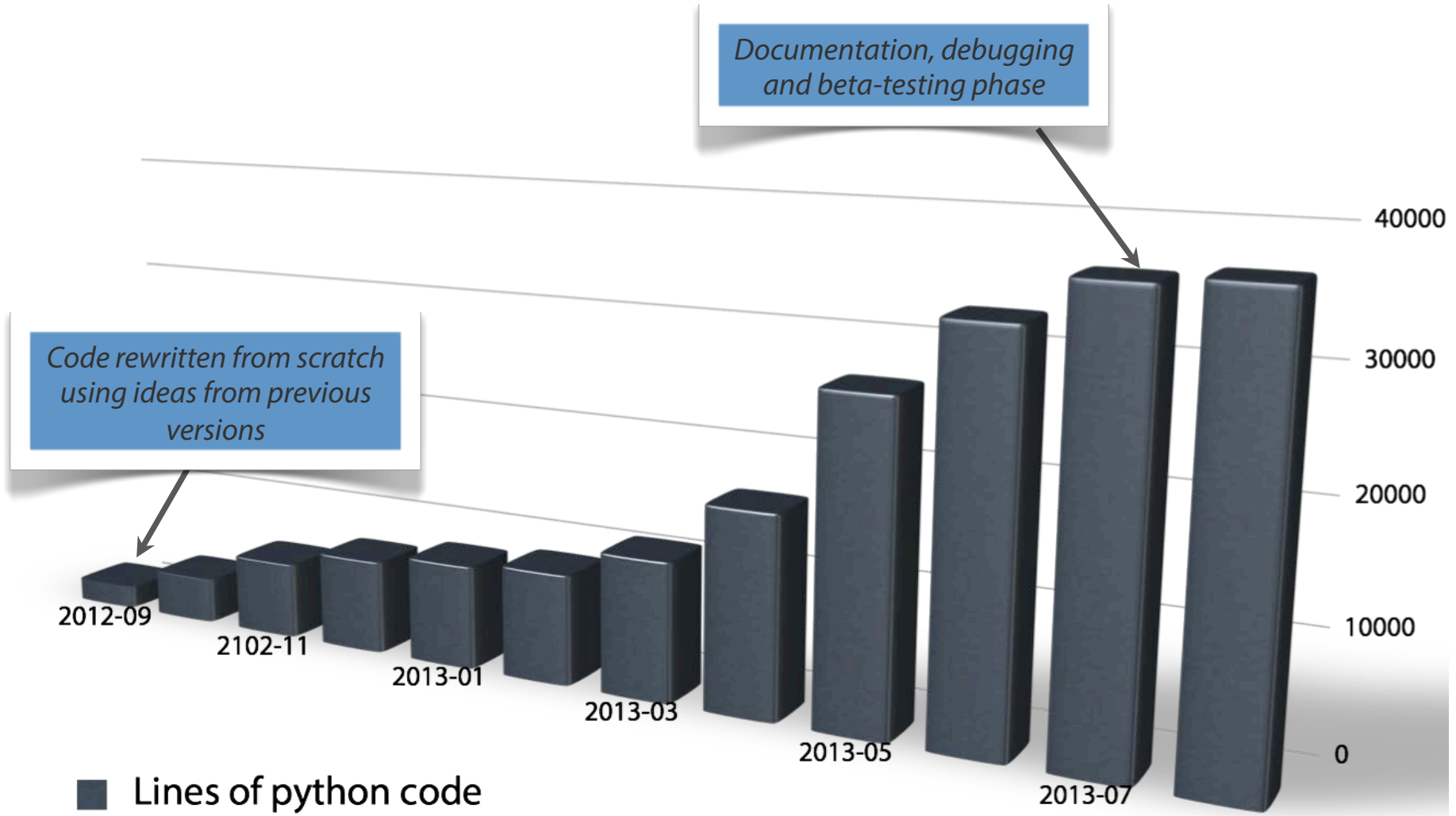
Full control of what is private, what is shared and what is public

Workflows

Powerful workflow engine for sequences of calculations

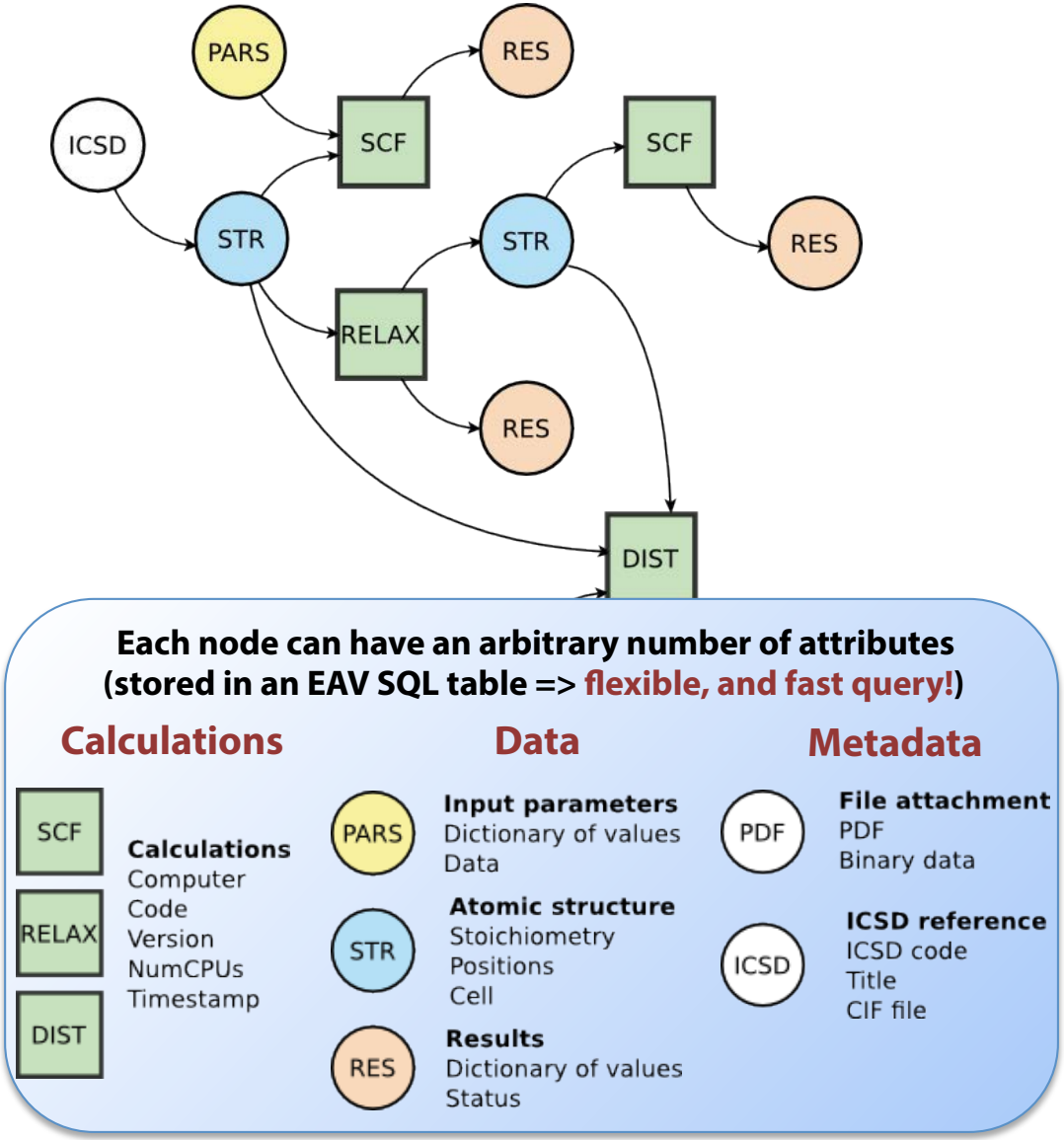
Calculations sync along the workflows, and wait for others to be ready

VERY ACTIVE DEVELOPMENT



Now: *active beta-testing phase + documentation + production*

AiiDA DATABASE INFRASTRUCTURE



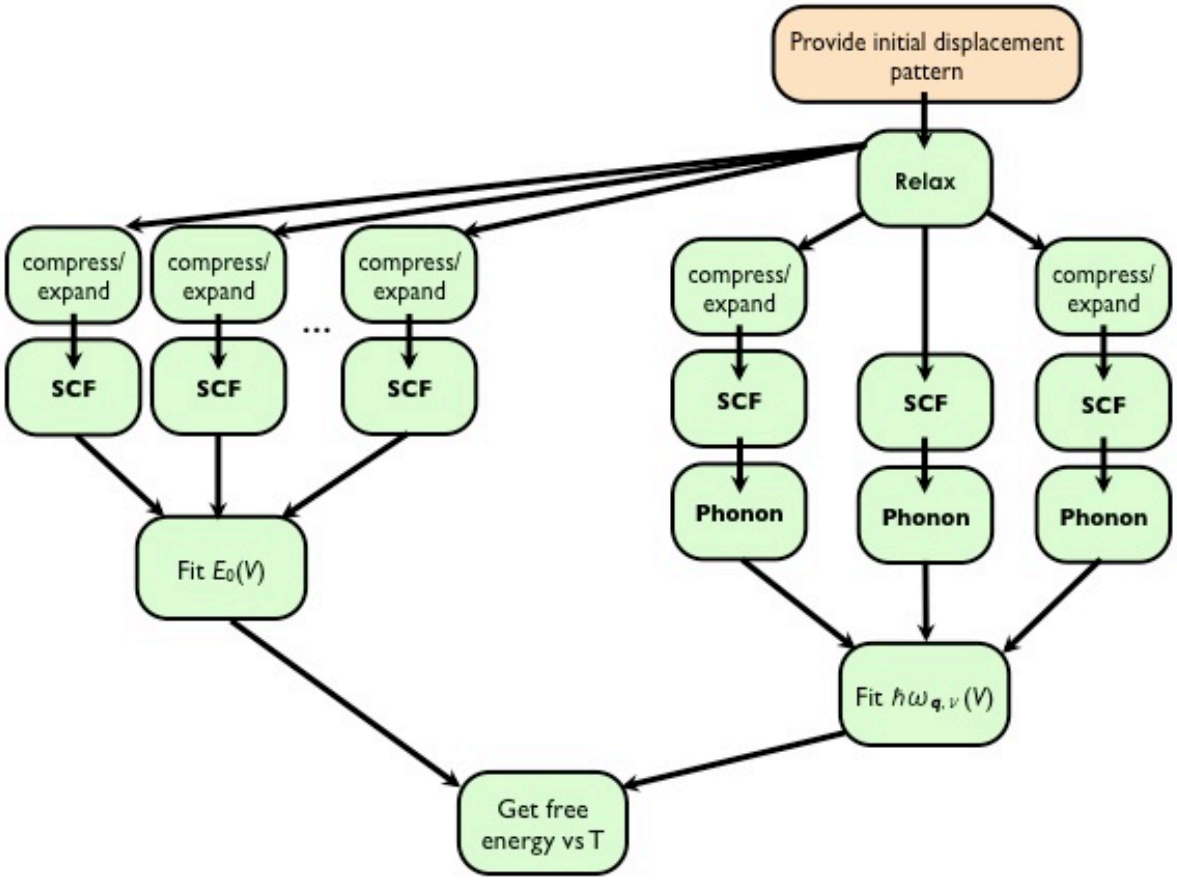
Nodes and links

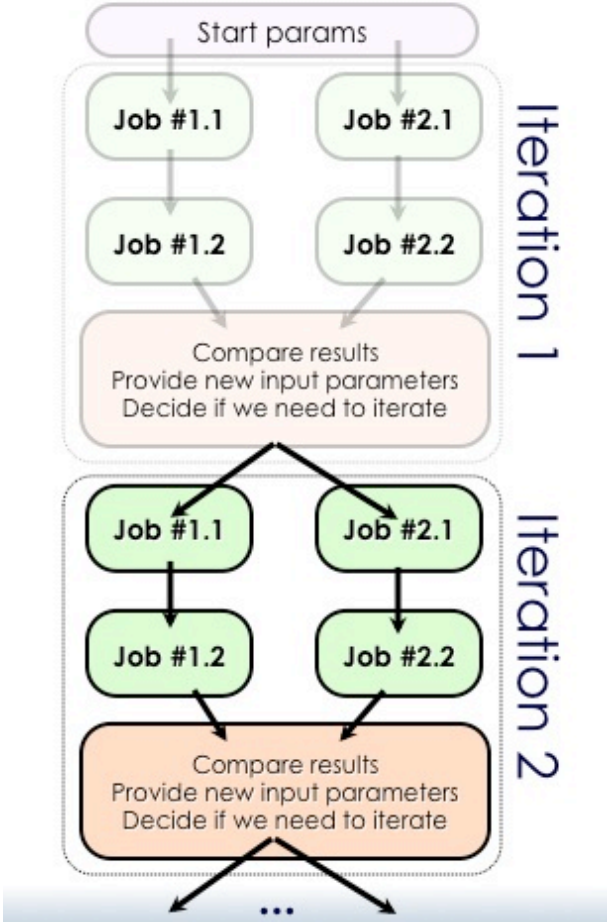
- **Input/output data and calculations: nodes of a graph**
- **Each node: row in a SQL table + folder for big files**
- **Links also stored in a SQL table => jobs provenance stored**

Transitive closure (TC) table

- **Links every node to any child or parent, for any number of "hoppings"**
- **Allows queries that traverse the graph**
- **Automatically updated using triggers**
- **Queries using TC faster than with graph DB backends! (tested vs. Neo4j)**

RAPID AND LONG-TERM REPRODUCIBILITY OF CALCULATIONS: WORKFLOWS AND DATA DEPENDENCY AND PROVENANCE



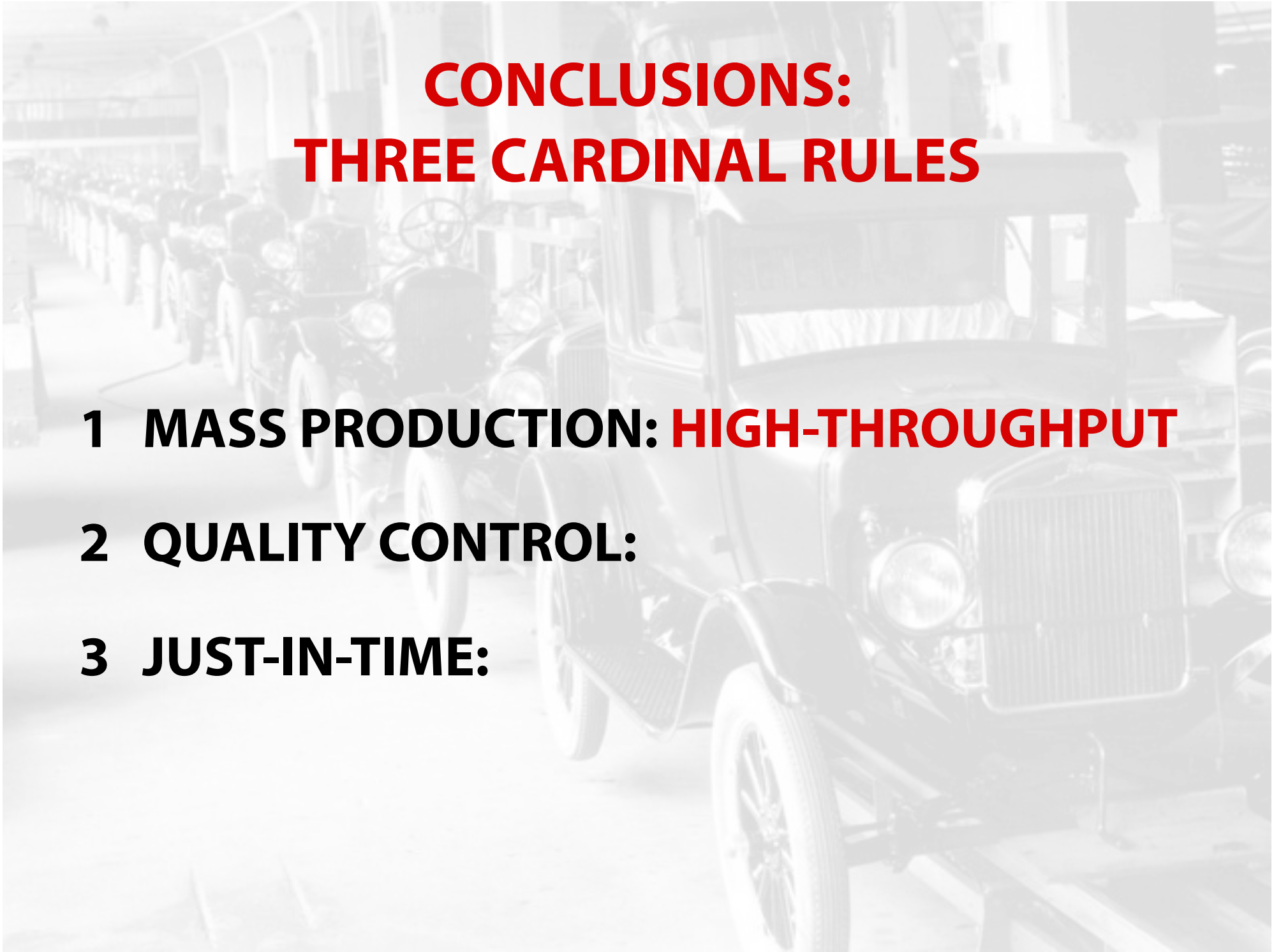


CONCLUSIONS:
THREE CARDINAL RULES

1 MASS PRODUCTION:

2 QUALITY CONTROL:

3 JUST-IN-TIME:

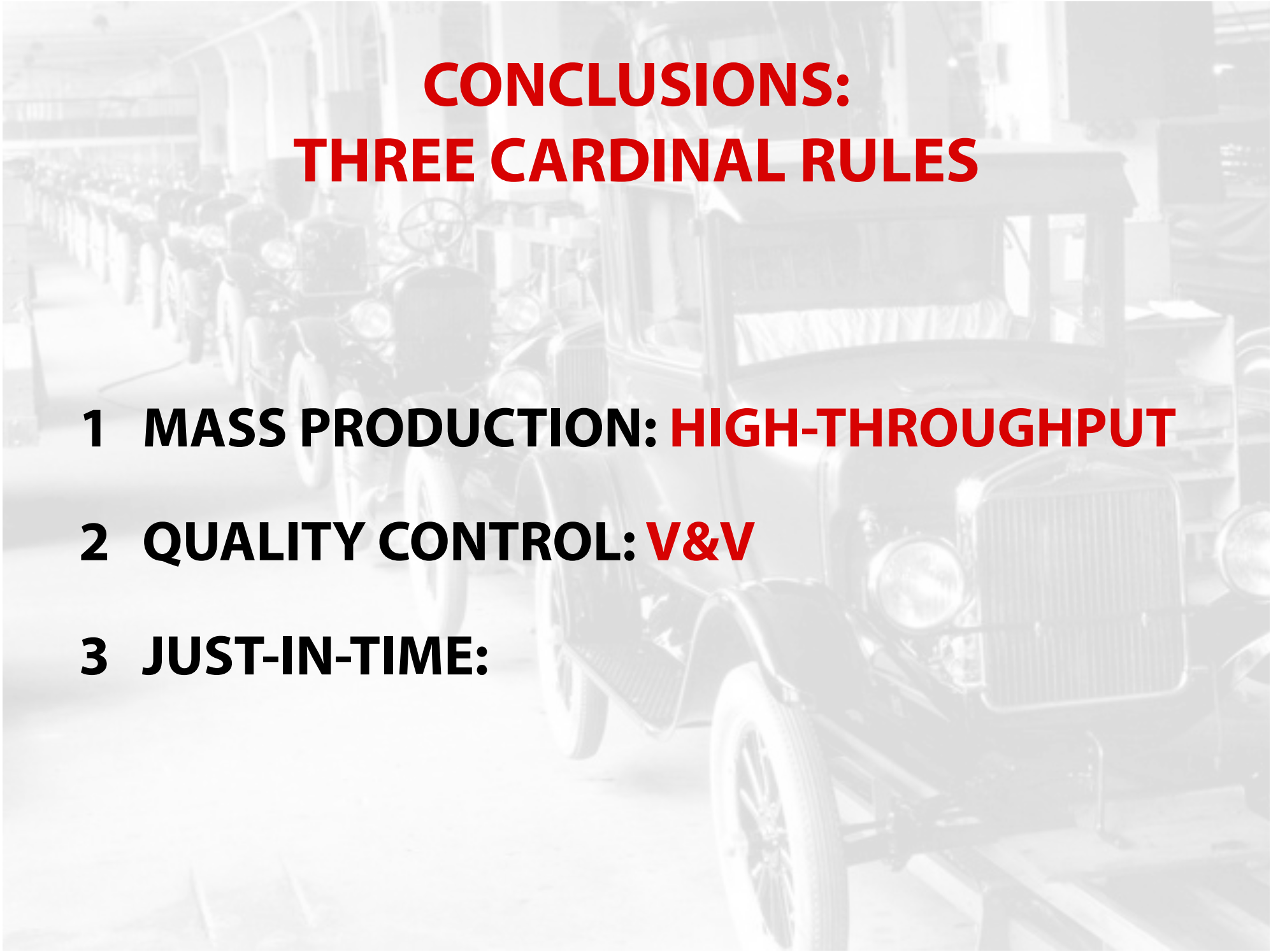


CONCLUSIONS:
THREE CARDINAL RULES

1 MASS PRODUCTION: HIGH-THROUGHPUT

2 QUALITY CONTROL:

3 JUST-IN-TIME:

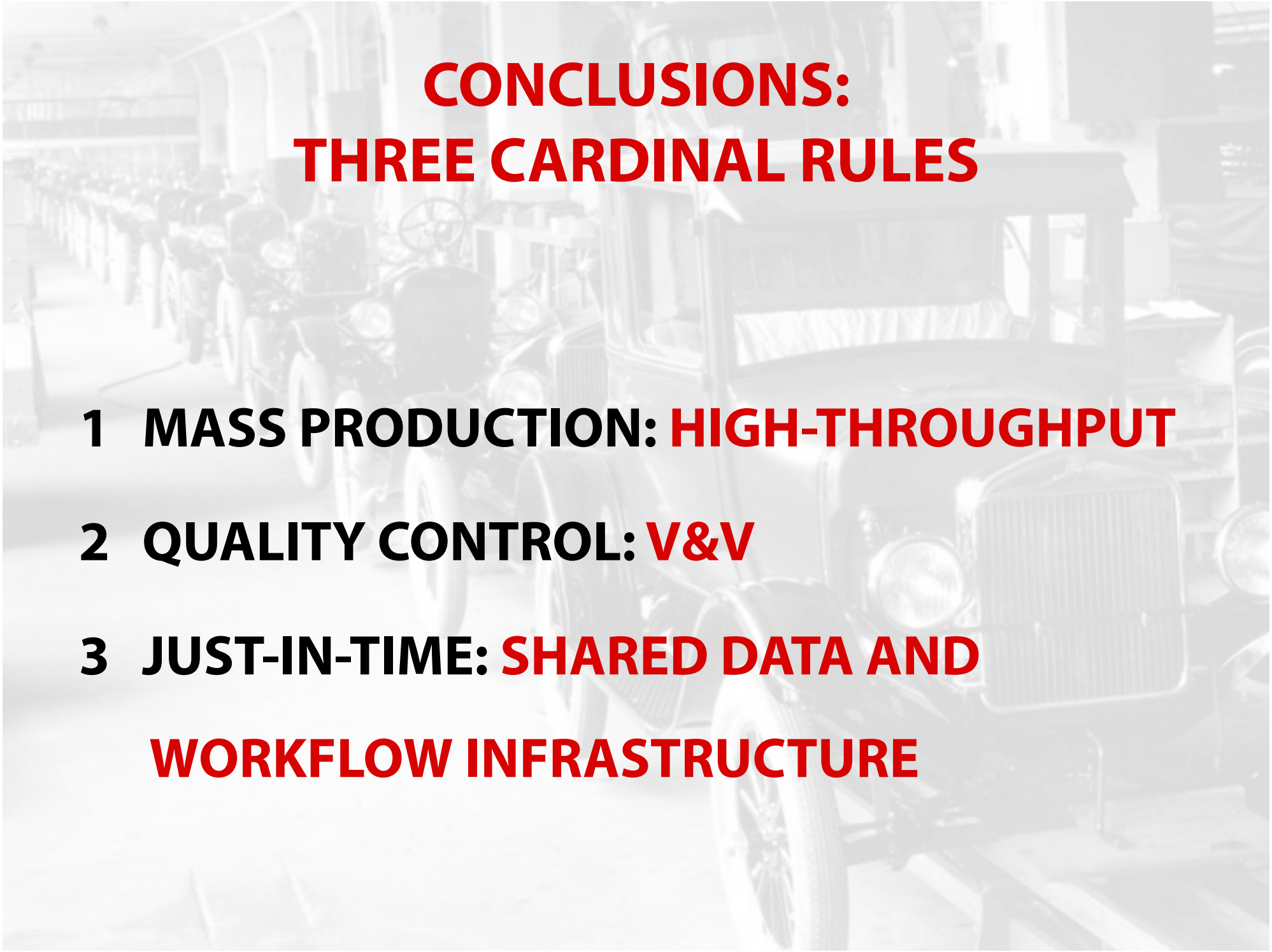


CONCLUSIONS:
THREE CARDINAL RULES

1 MASS PRODUCTION: HIGH-THROUGHPUT

2 QUALITY CONTROL: V&V

3 JUST-IN-TIME:



CONCLUSIONS:
THREE CARDINAL RULES

1 MASS PRODUCTION: HIGH-THROUGHPUT

2 QUALITY CONTROL: V&V

3 JUST-IN-TIME: SHARED DATA AND WORKFLOW INFRASTRUCTURE

NOT ONLY TIMELY, BUT URGENT

THEOS

THEORY AND SIMULATION OF MATERIALS

Nicola Marzari
(EPFL)

Boris Kozinsky
(BOSCH RTC)

BOSCH

AiiDA

The team

Giovanni Pizzi
(EPFL)

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(EPFL)

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SGE plugin and beta-tester: Marco Dorigo (ICAMS - Bochum)
Beta-testers, documentation improvements: Marco Gibertini, Giovanni Borghi (THEOS EPFL)