Computational tools in soft matter and mesoscale science … and some other stuff

Peter Littlewood

Associate Lab Director

Physical Sciences and Engineering

Trends

- Computation and theory traditionally used to validate models/theories with broad compass and little materials specificity
- Increasing use of computation to design particular experimental outcomes, or make extensive surveys of phase space – “materials by design”, “materials genome”,
- Nanoscale experimental probes
- Complexity, multi-functionality, multi-scale
- Big data and convergence of experiment and simulation
- Science drivers: energy is different from IT

Trend 1: Materials by design Materials Genome Initiative

The Materials Genome Initiative is a new, multi-stakeholder effort to develop an infrastructure to accelerate advanced materials discovery and deployment in the United States. Over the last several decades there has been significant Federal investment in new experimental processes and techniques for designing advanced materials. This new focused initiative will better leverage existing Federal investments through the use of computational capabilities, data management, and an integrated approach to materials science and engineering.

http://www.whitehouse.gov/mgi

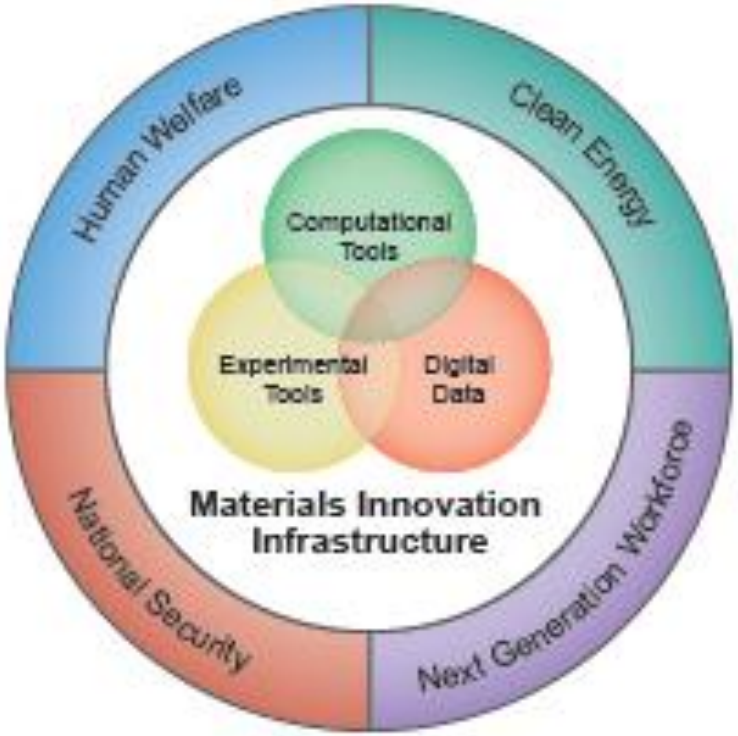


Figure 3: Initiative overview

Materials by design: genomics?

Genomics must be grounded in theory: the human genome initiative depends fundamentally on the “central dogma” of DNA coding. This is both the fundamental **theory** of biology and an **algorithm**

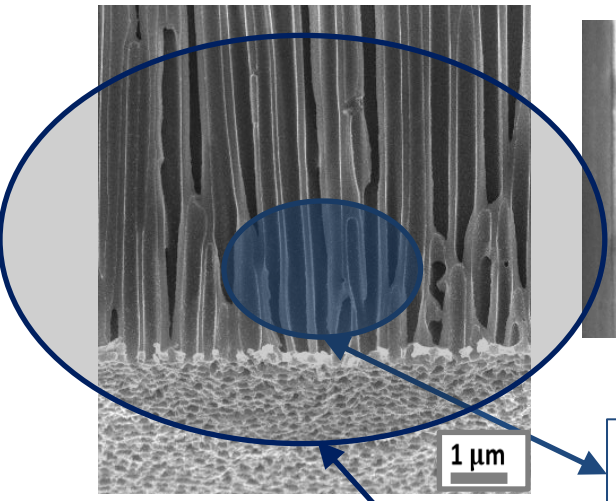
Materials genomics derives its validity from the Schrodinger equation – but this is not (yet) an instruction set

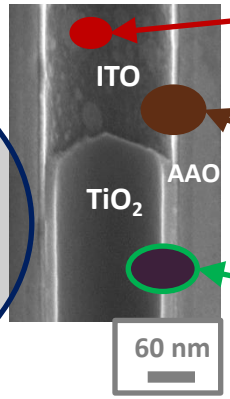
Robert Laughlin (Nobel lecture)

Many materials genomes …. Needs emerging from workshops

- Predictive models of fabrication, growth, etching, anodisation, deposition, ….
- Multiscale integration and design
- Simultaneous modeling/experiment
- Rapid materials surveys

Trend 2: multiscale modelling





Prediction of new materials and structures on the atomic scale, including interfaces, growth and defects

Excited state calculations for electron transfer and photon-mediated transitions

Accurate intermolecular potentials to model structure and dynamics on nanoscale

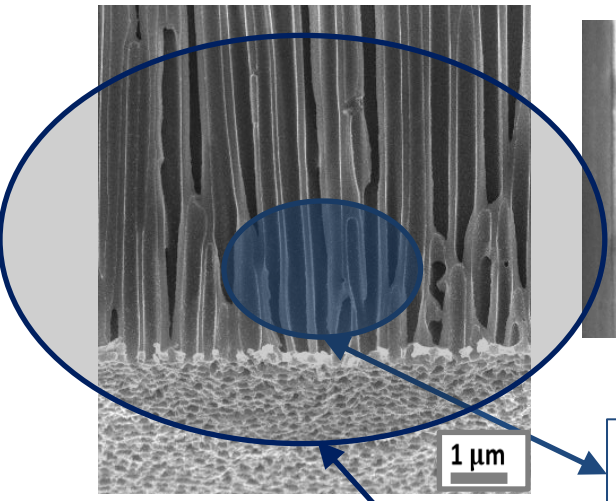
Semi-classical models of electrical and particle transport on mesoscale

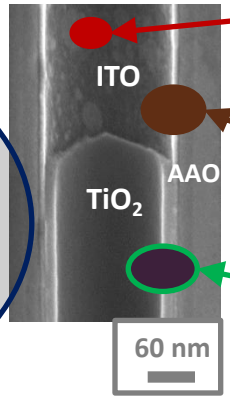
Effective theories of inhomogeneous media: elastic, fluid and electrical transport

- Each box requires new investment in methods, theory and computation
- Joining up the boxes is as important as the investment in any single piece
- We must curate both data and software
- Design choices driven by application target

Demands a collective corporate effort linking computation, methods, software, and data guided by an engineering goal

Trend 2: multiscale design ….





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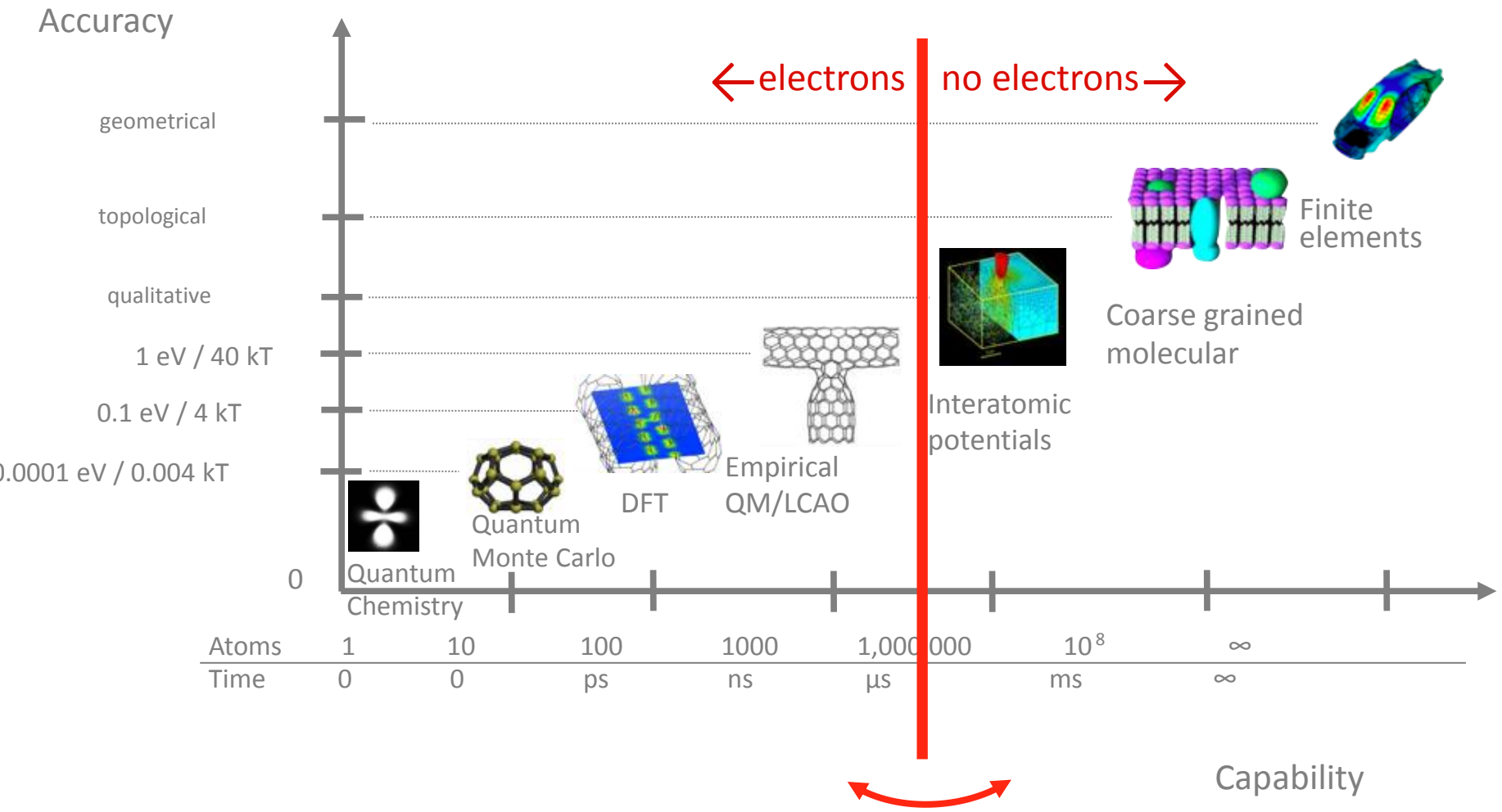
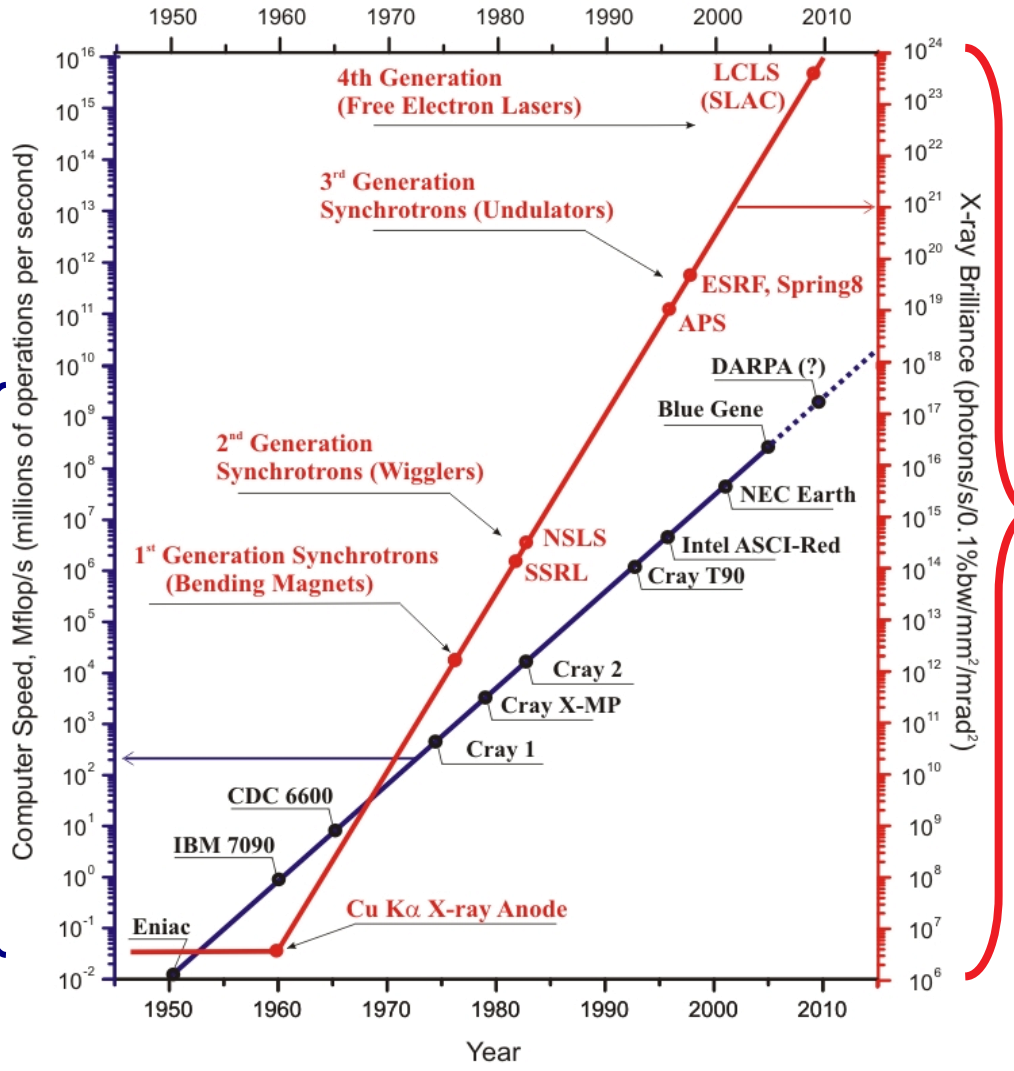
Multiple scales of materials modelling



GAP in accuracy and speed

Trend 3: Big data

Computers: 12 orders of magnitude in 6 decades

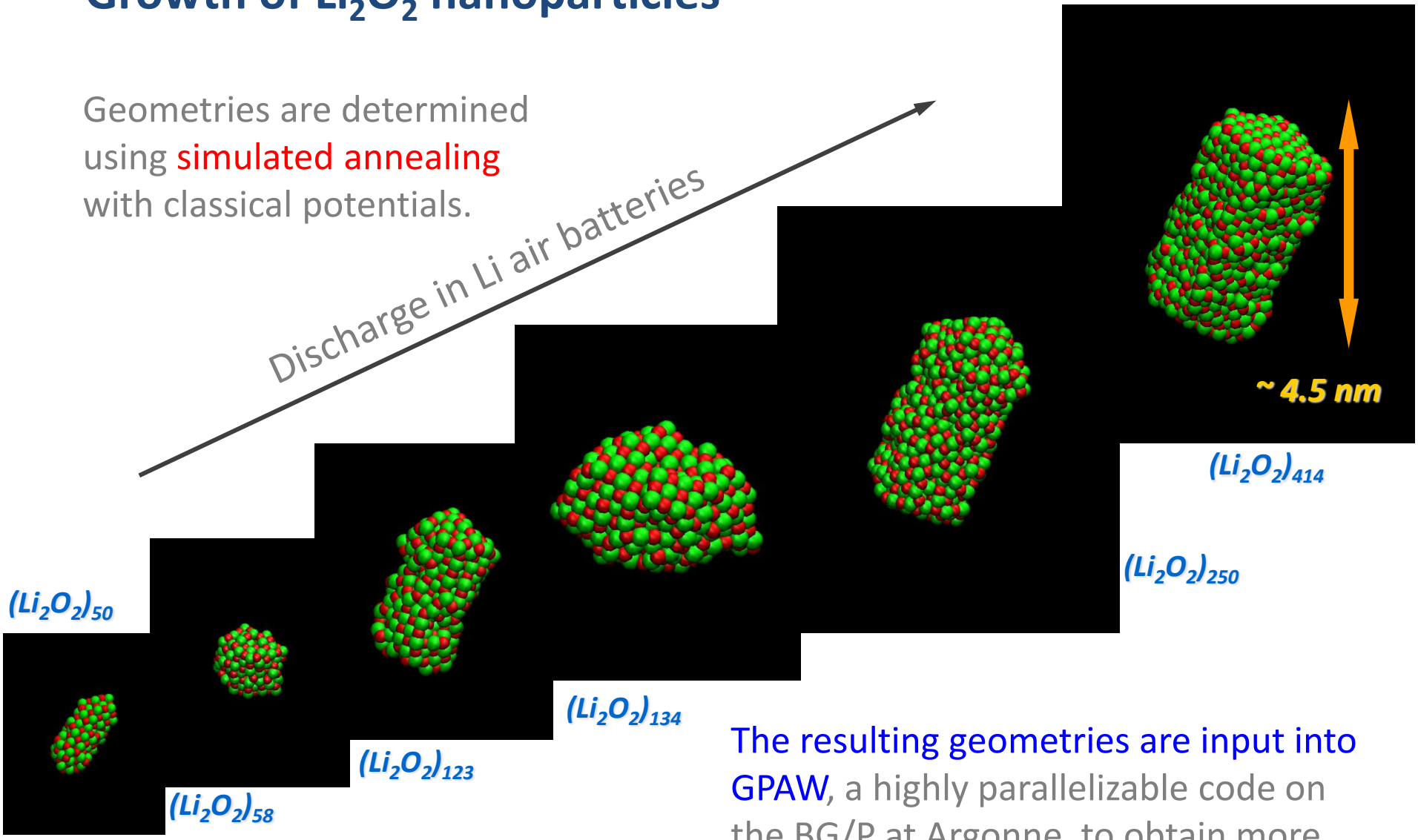


Light sources: 18 orders of magnitude in 5 decades

Some current applications

Growth of Li_2O_2 nanoparticles

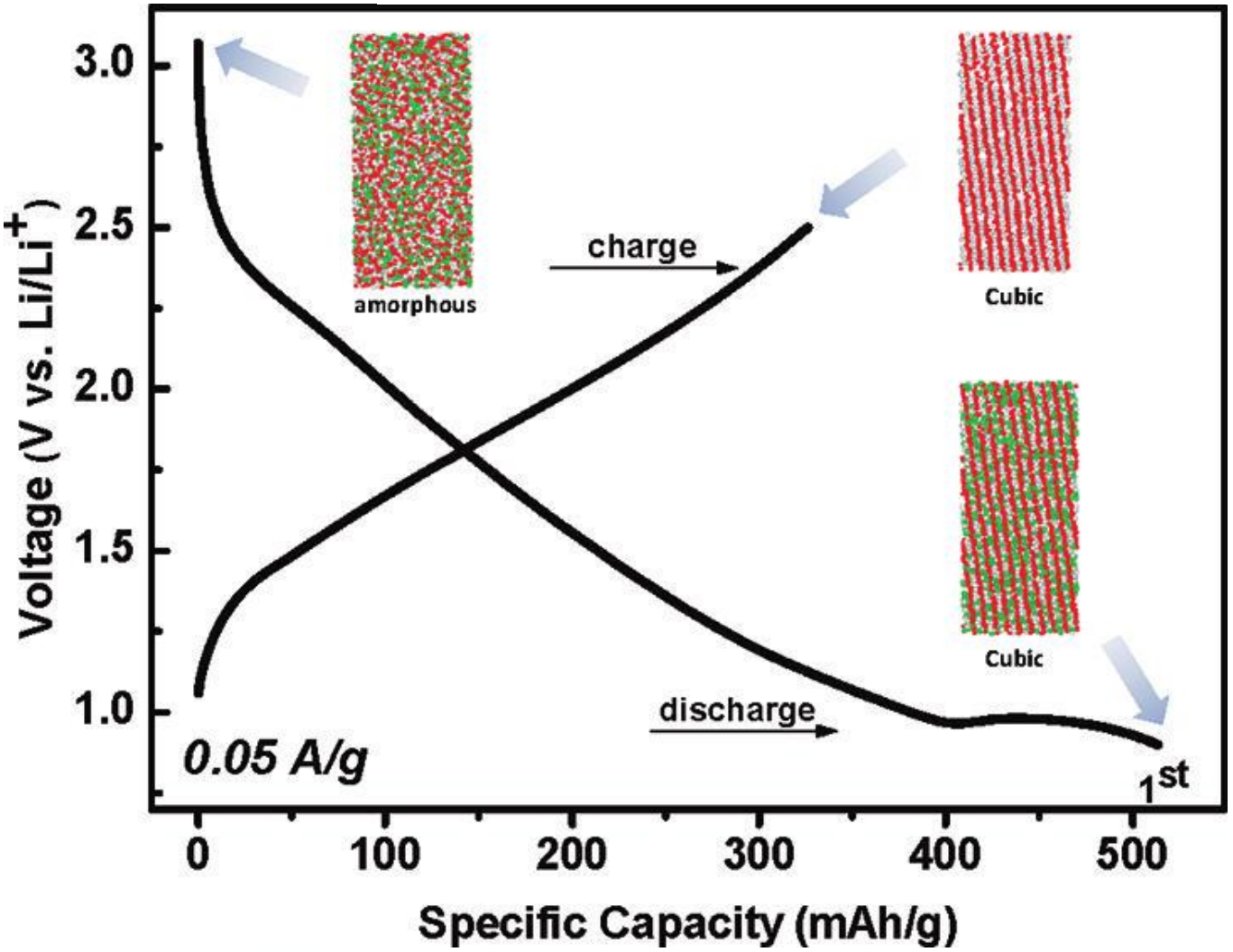
Geometries are determined using simulated annealing with classical potentials.



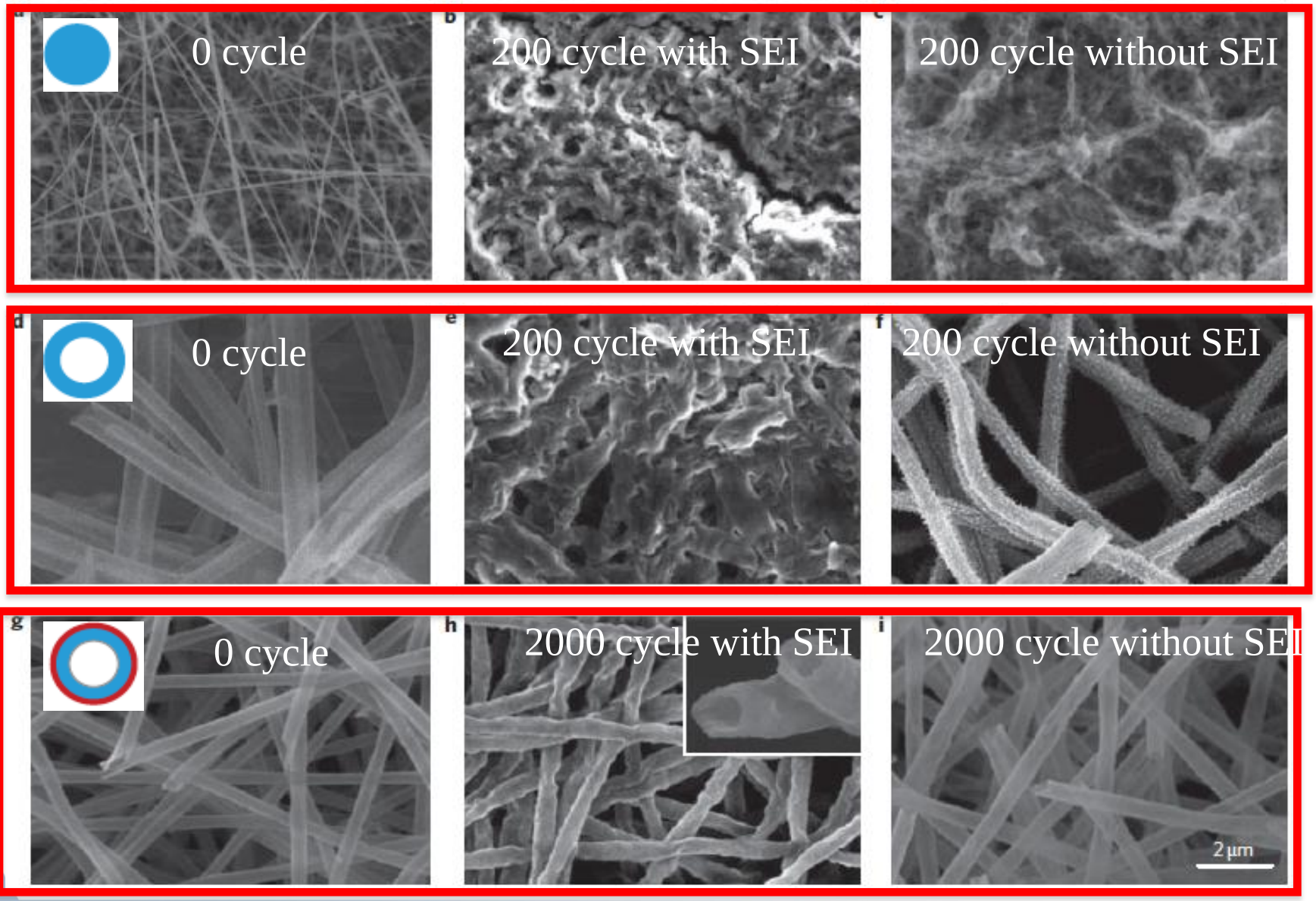
The resulting geometries are input into GPAW, a highly parallelizable code on the BG/P at Argonne, to obtain more accurate energetics.

Self-Improving Anode for Lithium-Ion Batteries Based on Amorphous to Cubic Phase Transition in TiO_2 Nanotubes

dx.doi.org/10.1021/jp210793u | J. Phys. Chem. C 2012, 116, 3181–3187

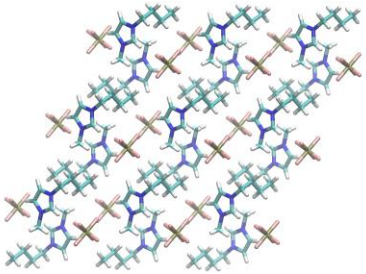


Si nanowires as anodes in Li-ion battery: Yi Cui

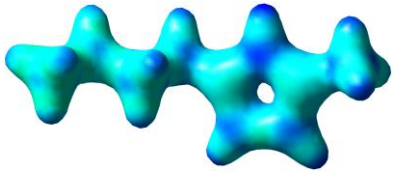


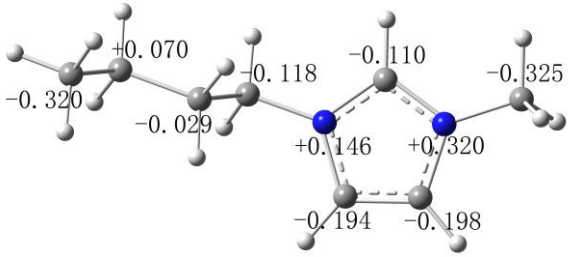
Predictive Simulation of Ionic Liquid Properties

- **Computational framework for automatic and rapid prediction of liquid phase properties**



Short AIMD simulation

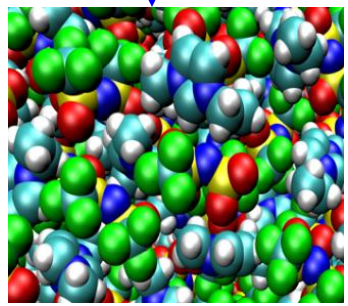




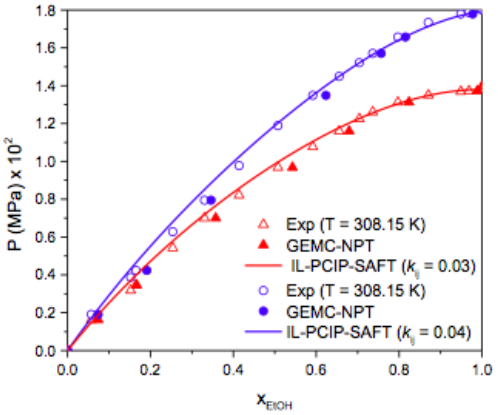
crystalline or liquid phase

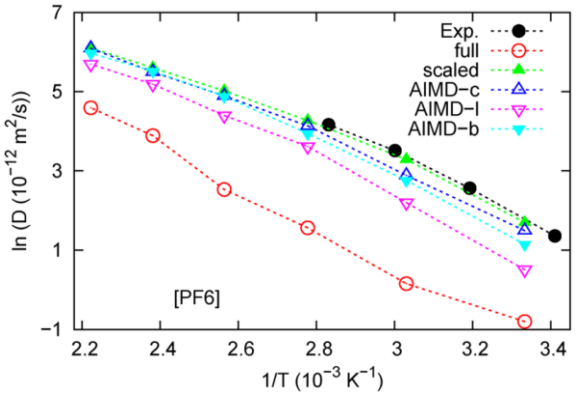
electrostatic potential and structure

partial charges, force field parameters



MD, MC simulation





predicted properties

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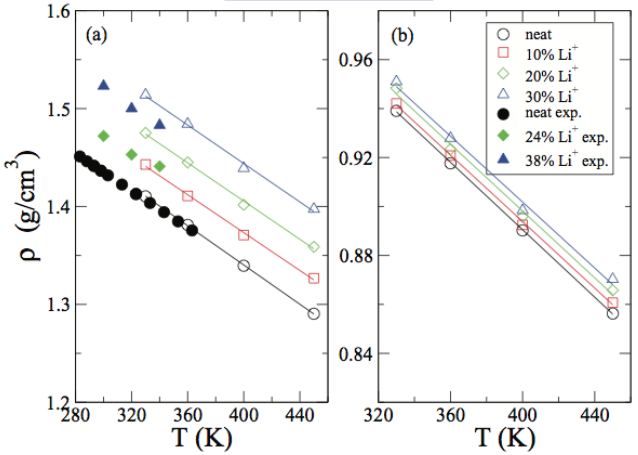
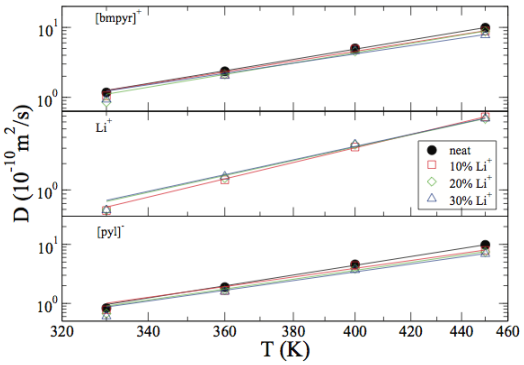
What can be computed?

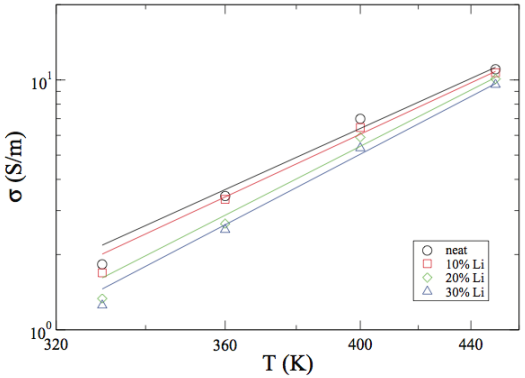
density



diffusivity



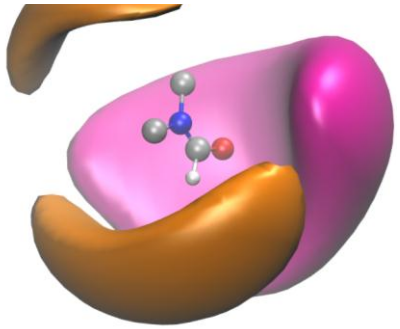
conductivity



Melting points, enthalpy of fusion

IL	T_m (K) Calc.	T_m (K) Exp.	ΔH_f (kcal mol^{-1}) Calc.	ΔH_f (kcal mol^{-1}) Exp.
[BMIM][PF6]	284 ± 1	284[a]	4.50 ± 0.18	4.75[d] 4.76[e] 4.68[f]
[BMMIM][PF6]	296 ± 1	313[b]	4.04 ± 0.16	4.08[g]
[EMIM][PF6]	330 ± 1	338[c]	4.23 ± 0.13	4.27[d]
[EMMIM][PF6]	424 ± 1	474[c]	4.32 ± 0.18	

liquid structure



Plus many more!

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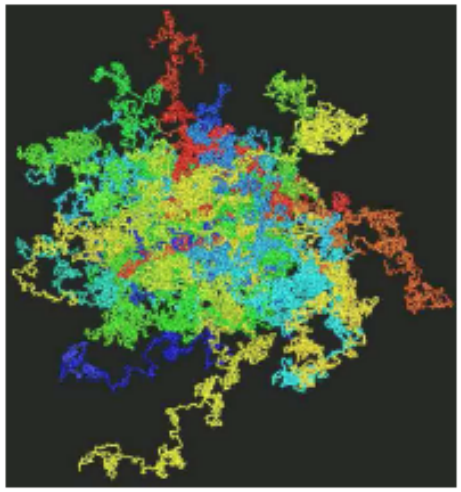
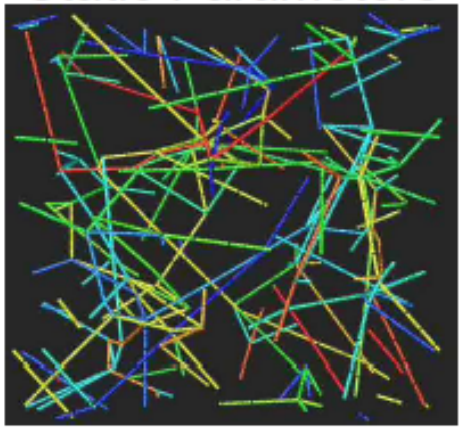
Goal: *Ab initio* polymer rheology predictions via DSM

MD simulation



⇒

Determination of Static Parameters



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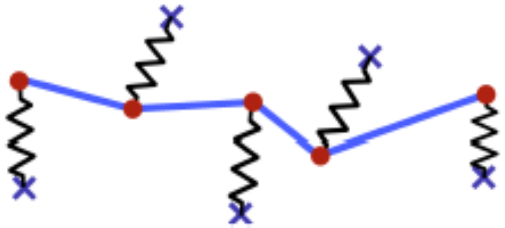
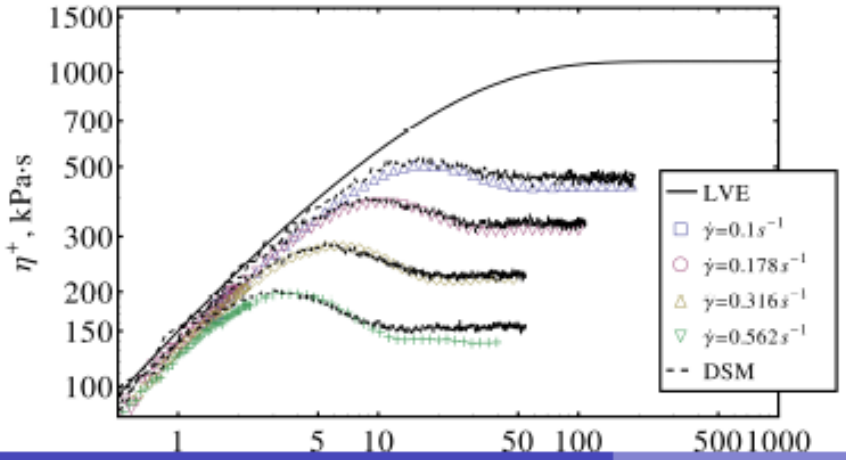
DSM model



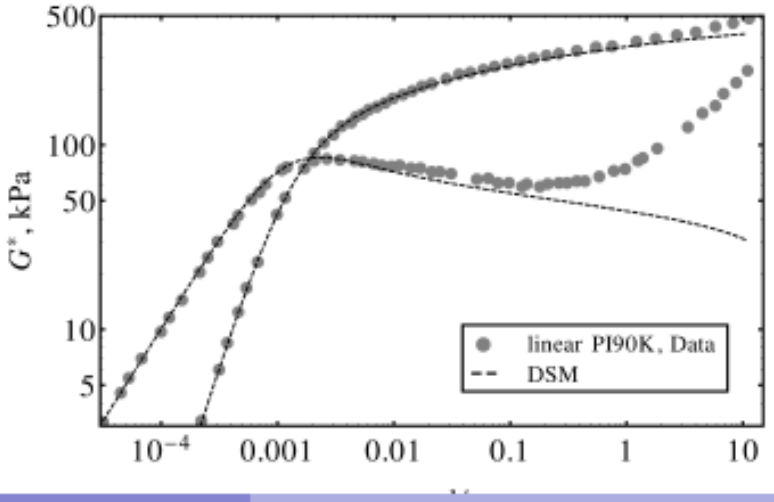
⇓ Adjust single parameter

Non-linear rheology predictions, 56kDa star-branched melt



⇐

Linear modulus predictions



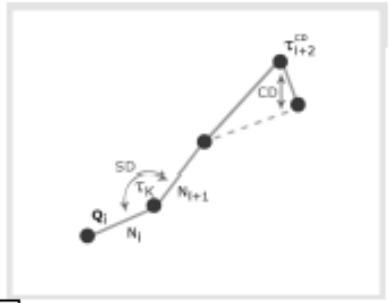
Goal: Engineering rheology of PDMS Gels swollen with entangled PDMS solvent

- Polydisperse components.
- Unknown fraction of dangling strands.

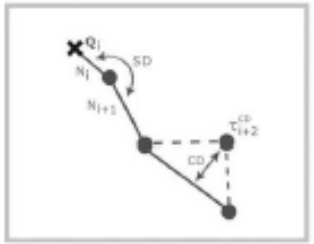
Modeling

- Each component simulated with self-consistent mean field (blend CD).

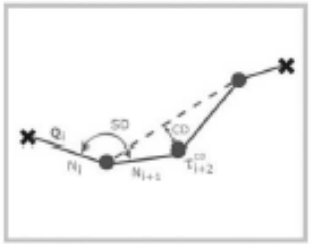
entangled solvent

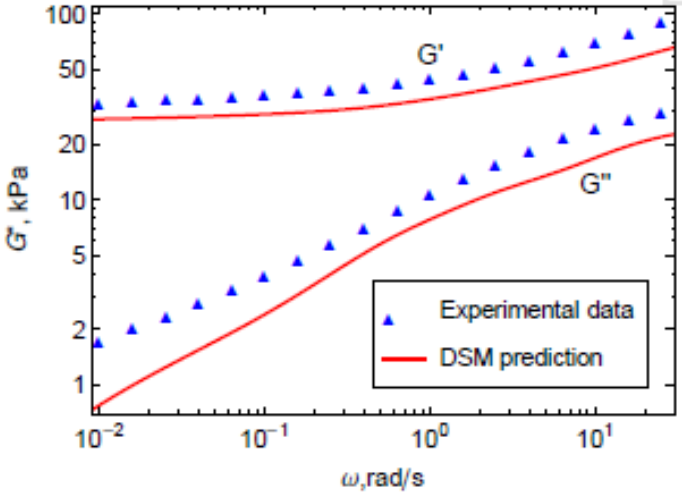


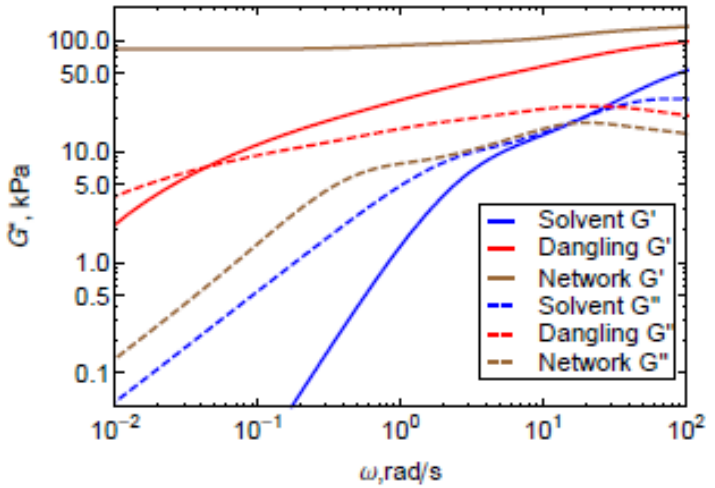
dangling end



entangled network strand

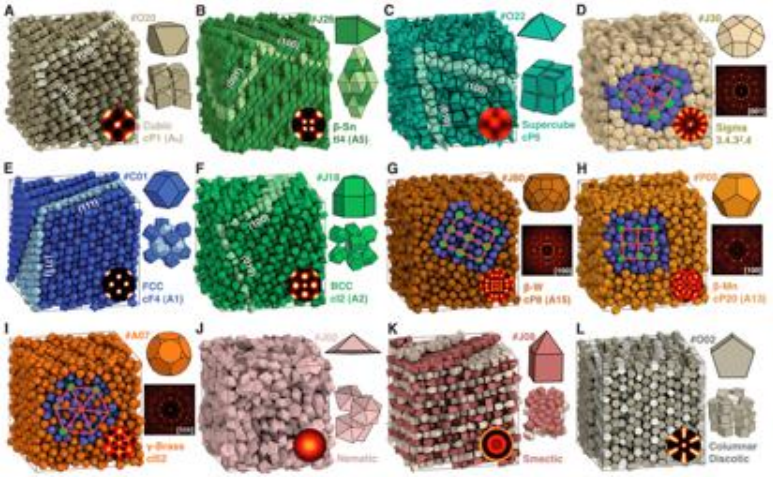




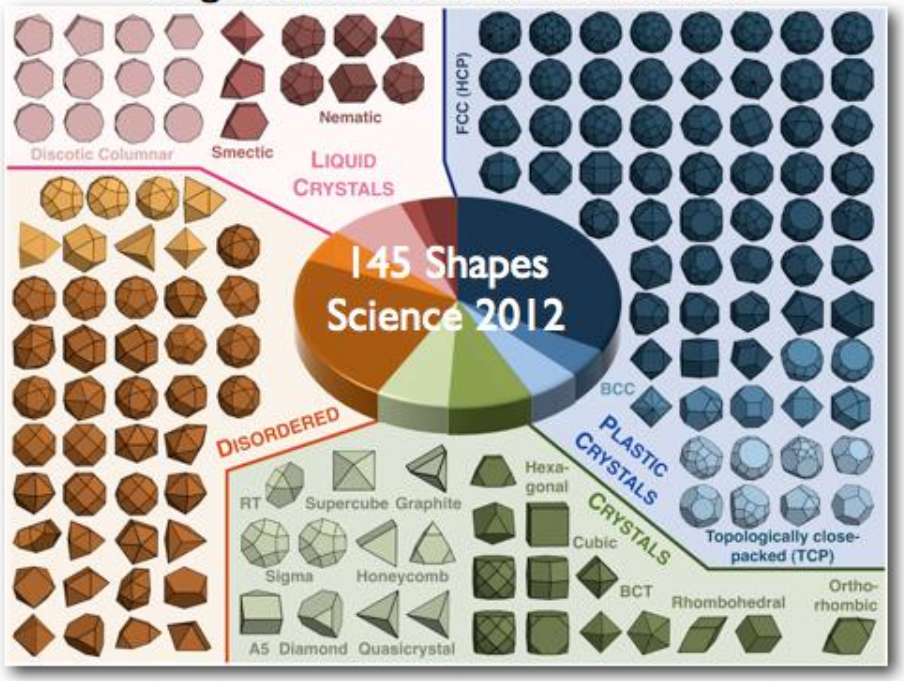


Towards Predictive Colloidal Crystal Assembly

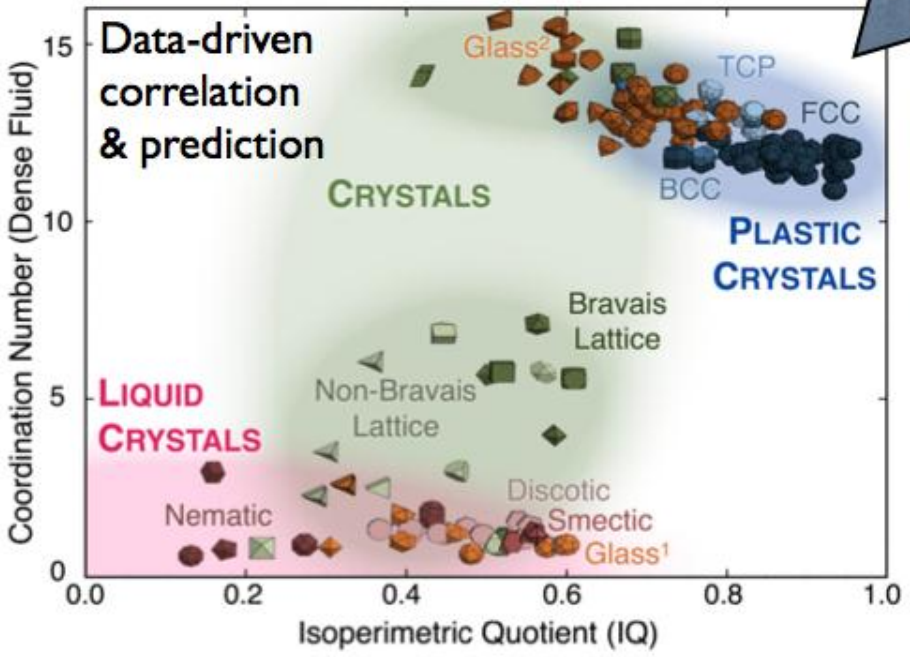
Simulations predict assemblies from shapes



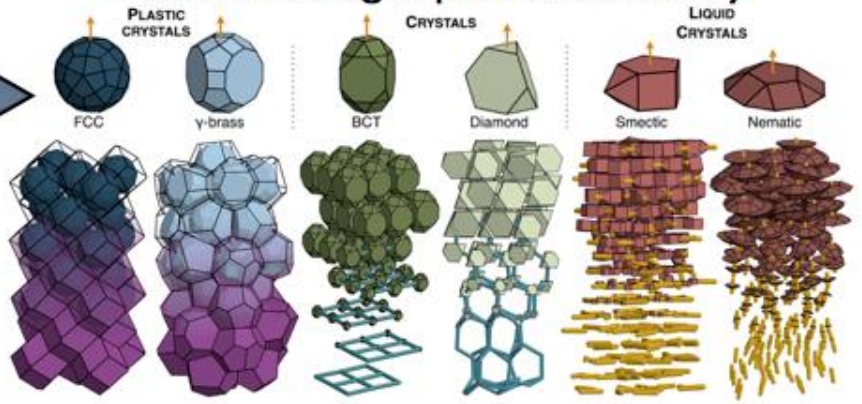
Huge data sets allow classification



Data-driven correlation & prediction

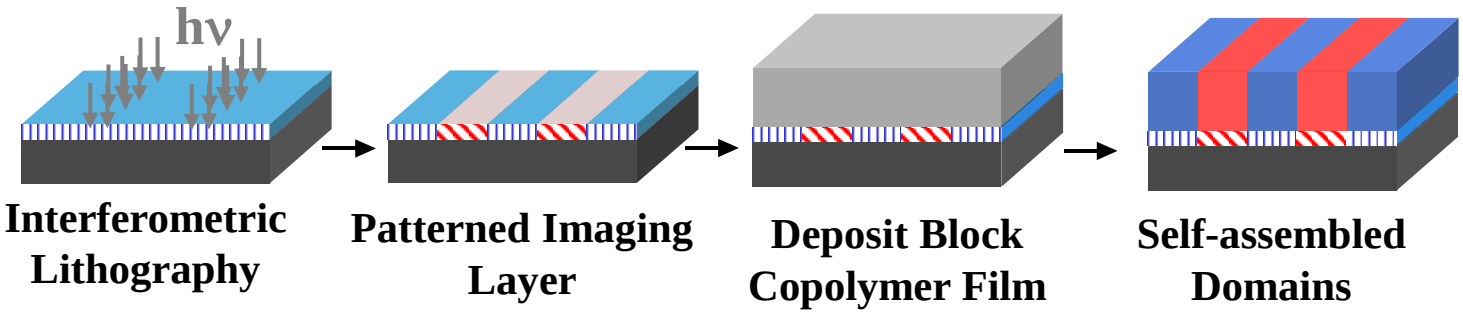


Understanding & predictive theory

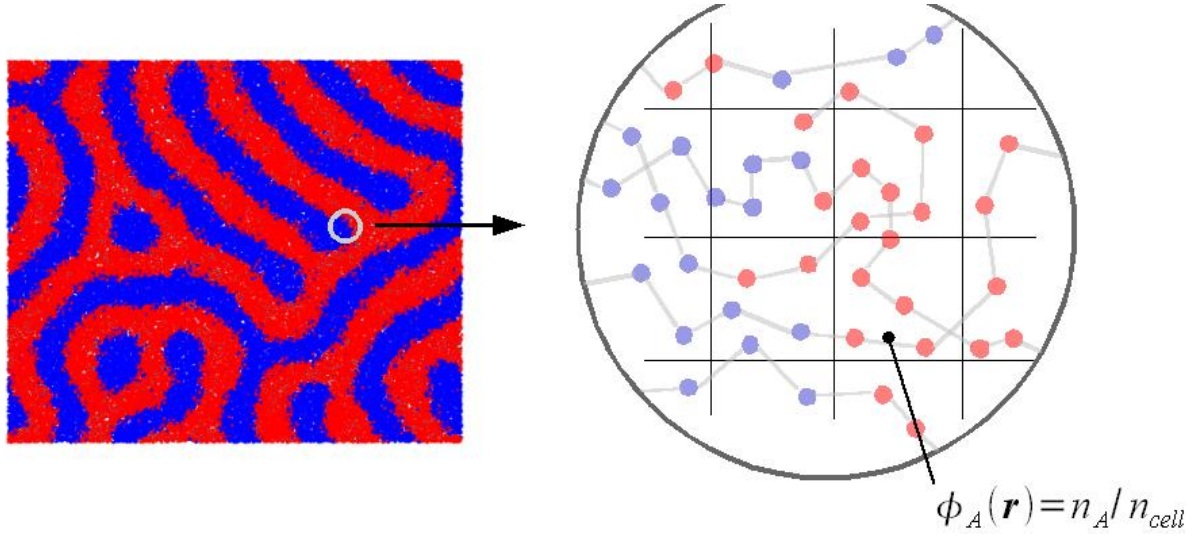


Damasceno, Engel, SCG, Science 2012

Lithographically directed self assembly of block copolymers – de Pablo

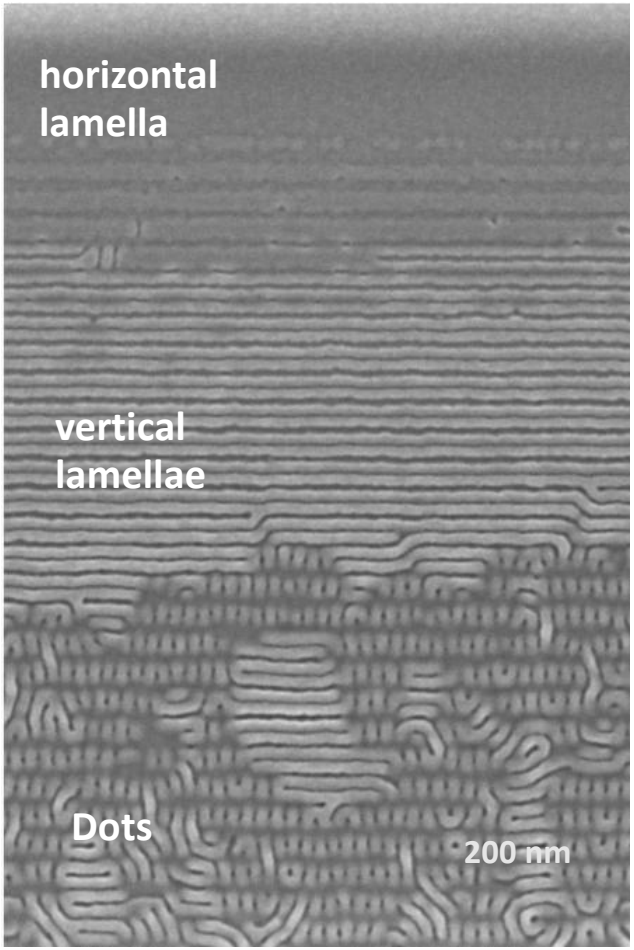


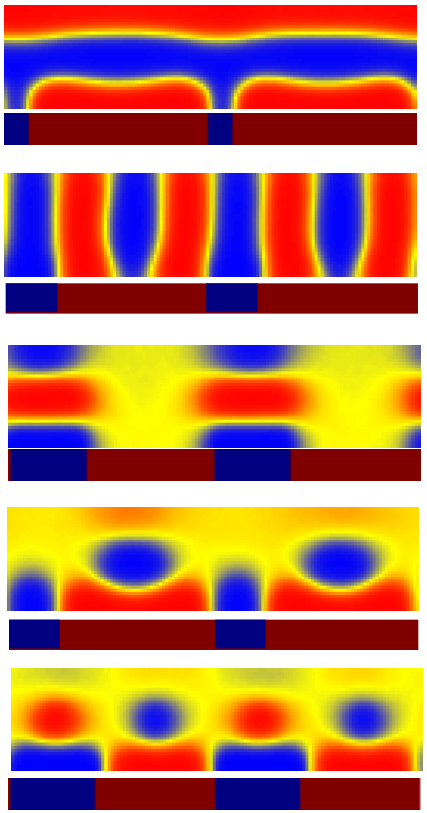
"Standard" MC simulation: entanglement means time scales are very long ....

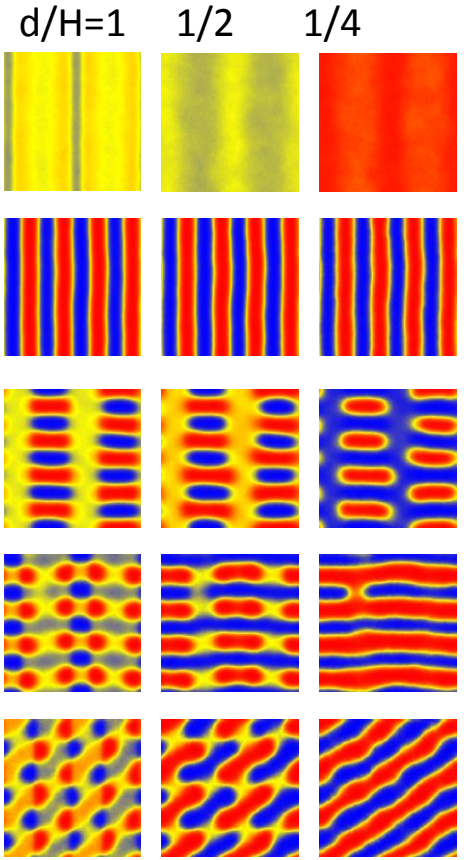


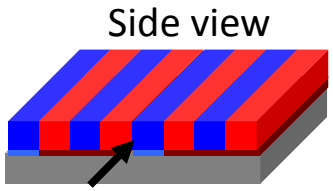
A Combinatorial Approach - Experiment

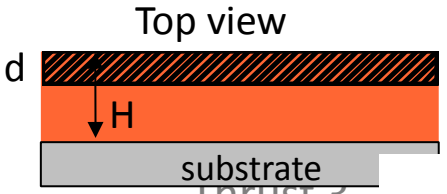
More than 400 combinations of parameters were considered, yielding five types of morphology:





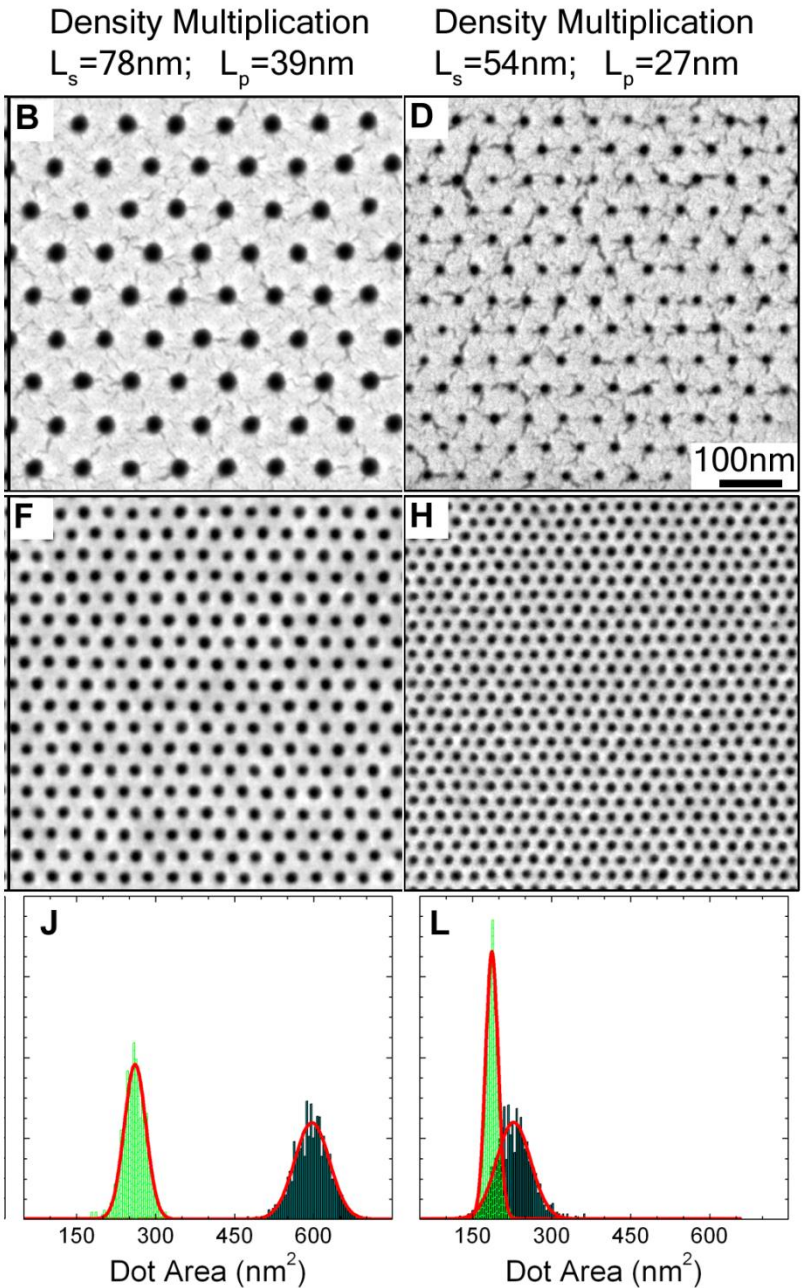


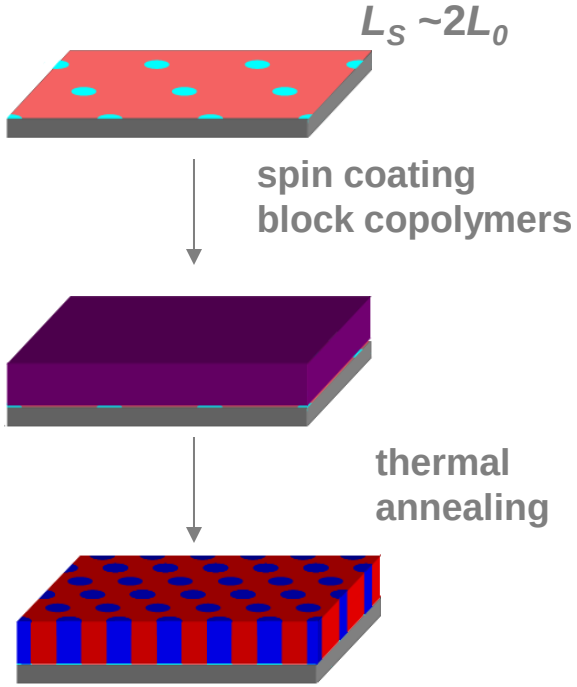




Detcheverry et al., *Macromolecules*, 2010

Multiplication of feature density (or interpolation)



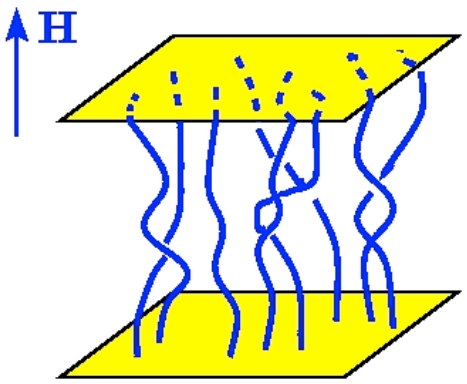


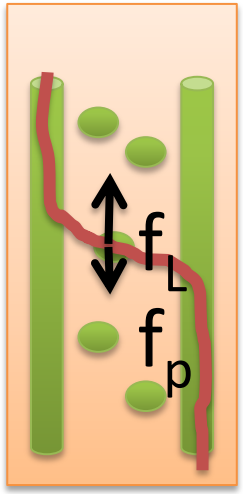
- **Density multiplication: factor of four**
- **Improved performance at limits of exposure tool**
- **PS-PMMA – limit ~13 nm features**

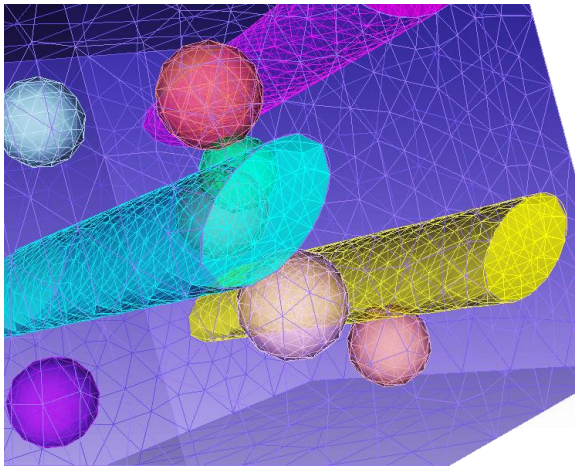
UW/HGST Collaboration

Ruiz, Nealey, de pablo et al., *Science* 2008

Better superconductors - design of vortex pinning for large current applications







$$\mathcal{F}_{GL} = \frac{1}{2}\int d^d x \left\{ \beta \left(\frac{\alpha}{\beta} + |\psi|^2 \right)^2 + \frac{\hbar^2}{m} \left| \left(i\nabla - \frac{2\pi}{\phi_0}\mathbf{A} \right)\psi \right|^2 + \frac{1}{4\pi}(\nabla \times \mathbf{A} - \mathbf{H})^2 \right\}$$

Time-dependent Ginzburg -Landau eqn.

$$\frac{\partial \Psi}{\partial t} = -\frac{\delta \mathcal{F}_{GL}}{\delta \Psi^*}, \quad \frac{\delta \mathcal{F}_{GL}}{\delta \mathbf{A}} = 0$$

Equations well understood: but contain long range forces, disjoint length scales, and need long times

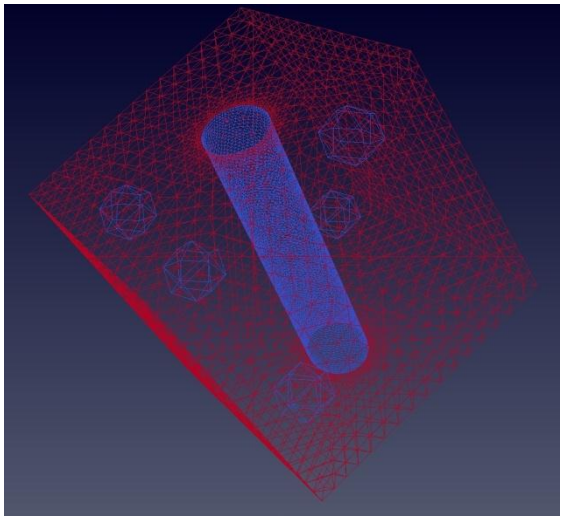
BES-SCIDAC – A Glatz, MSD

Computational Challenge: Complexity

Typical simulation complexity

- Simulations of $O(10^6)$ timesteps for reliable V values
- Sample volumes $O(10^{6}»)$ + meshes with cell size $O(10^{-1}»)$

  → *$O(10^9)$ degrees of freedom (DoF) per realization of pinning configuration μ.*



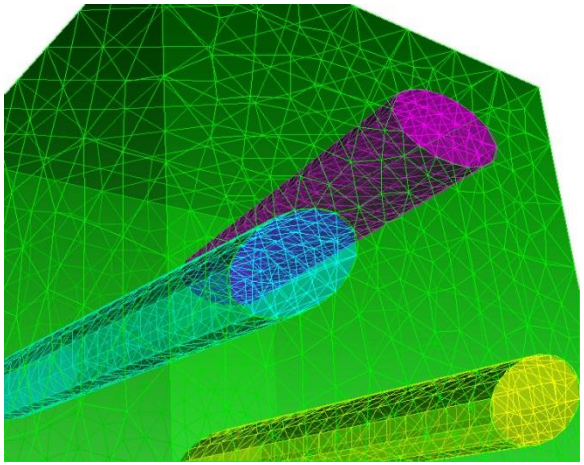
Computational demand for 10^3 flops per DoF per timestep

- 10 - 100h on full 100TFlop/s machine *at peak* for single μ
- Sampling J & μ increases demand by O(100)-O(1000) x

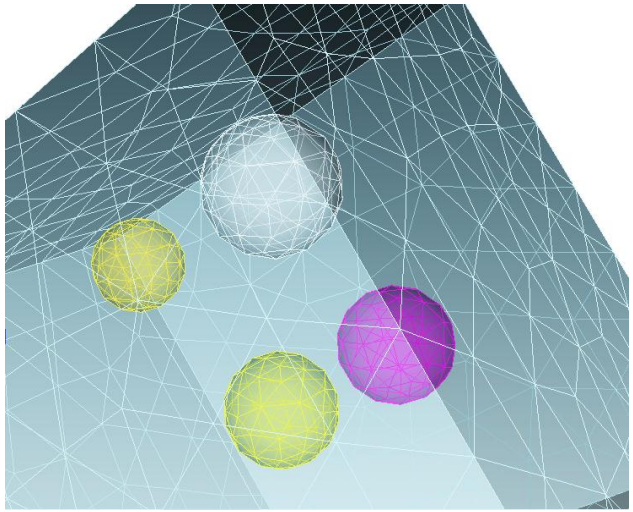
→ **Computational requirements**

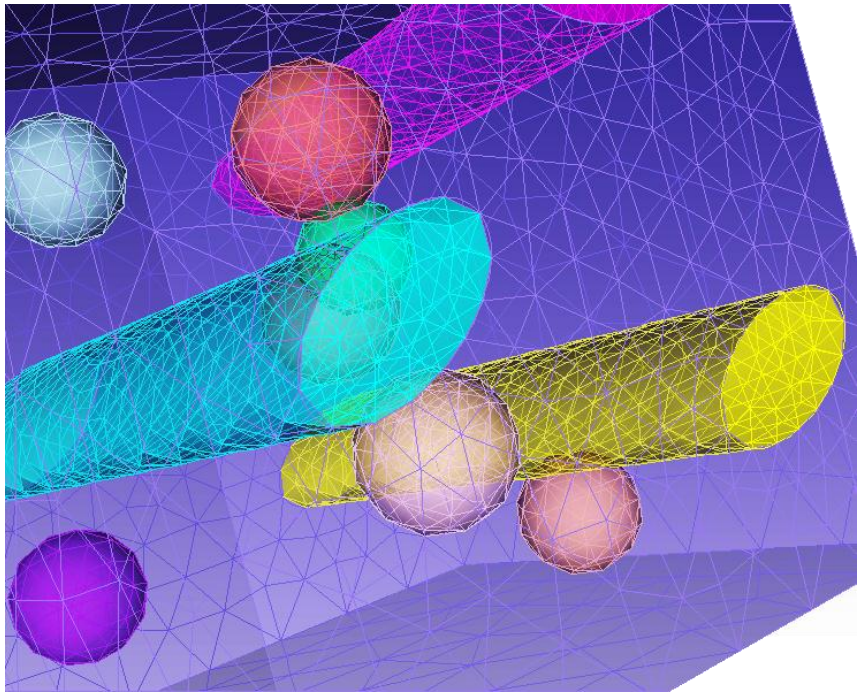
- Leadership-class hardware for computational optimization of pinning structures
- State-of-the-art sampling techniques to minimize the number of probed μ
- Automated meshing of materials with embedded pinning structures
- Fully implicit time-integration to circumvent the timestep size limitation
- Modern iterative methods to solve O(1B) system at each timestep in optimal time.

Computational Challenge: Meshing



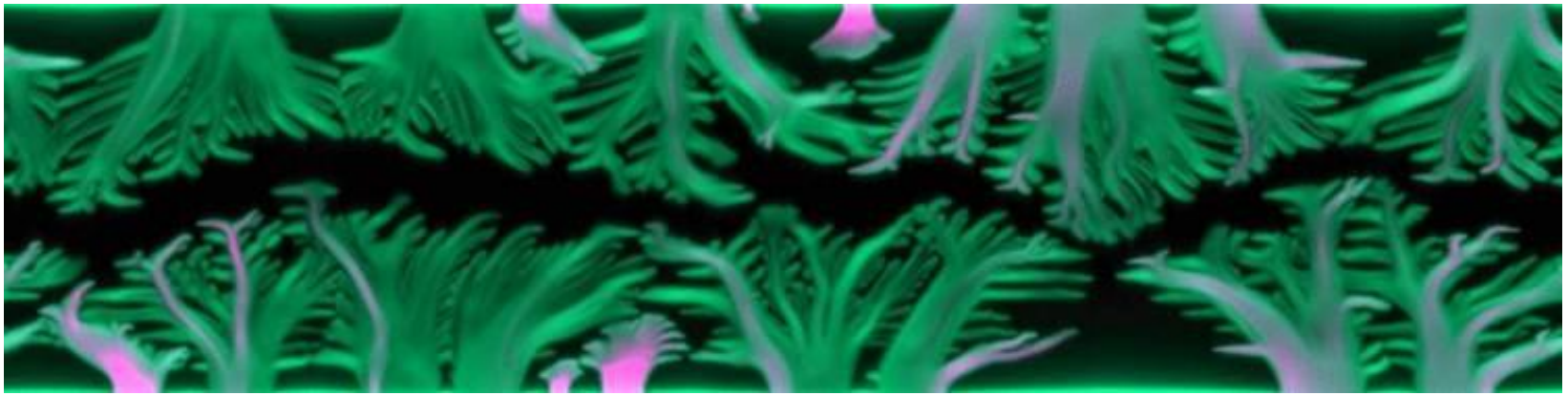
- mesh size needs to be smaller than the coherence length to capture to dynamics correctly
- near inclusions and defects mesh needs to be finer → *Adaptive meshing*
- increased precision by adaptive mesh refinement near vortices





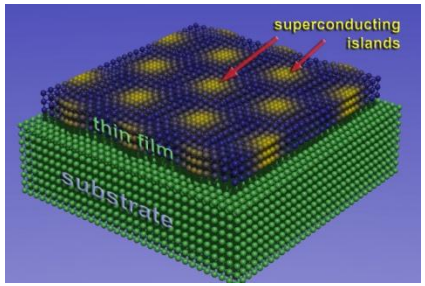
Extension of the TDGL formalism

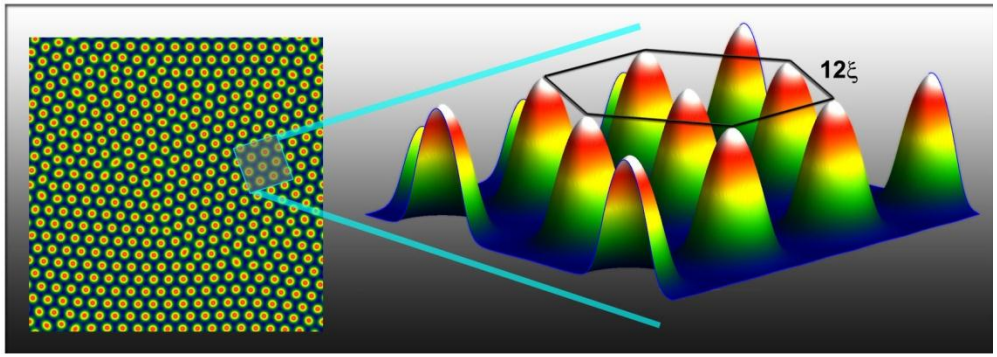
- Modeling of thermomagnetic avalanches



nonlinear magnetic flux diffusion equation coupled to thermal diffusion in 2D

- Coupling to elastic strain



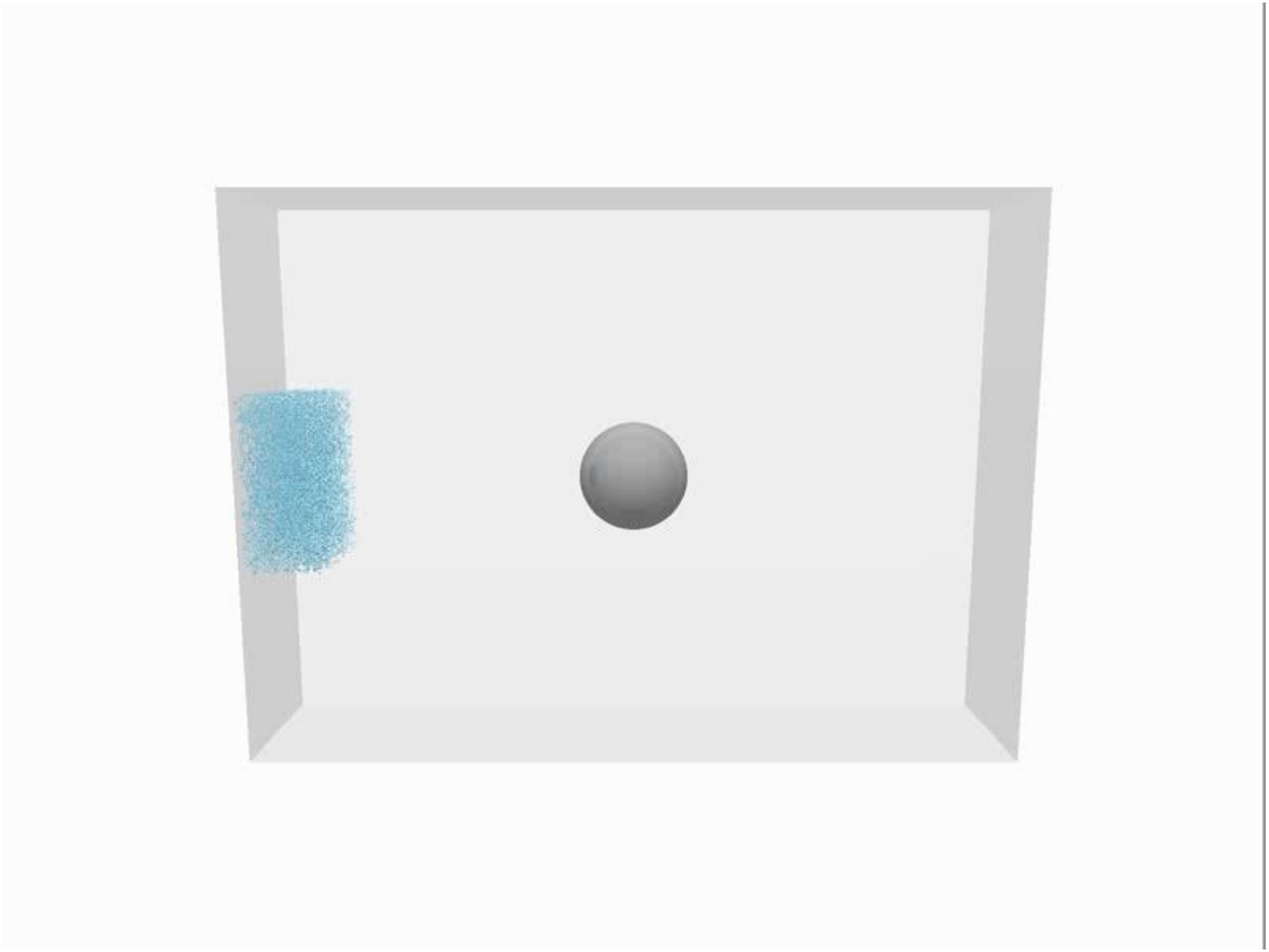


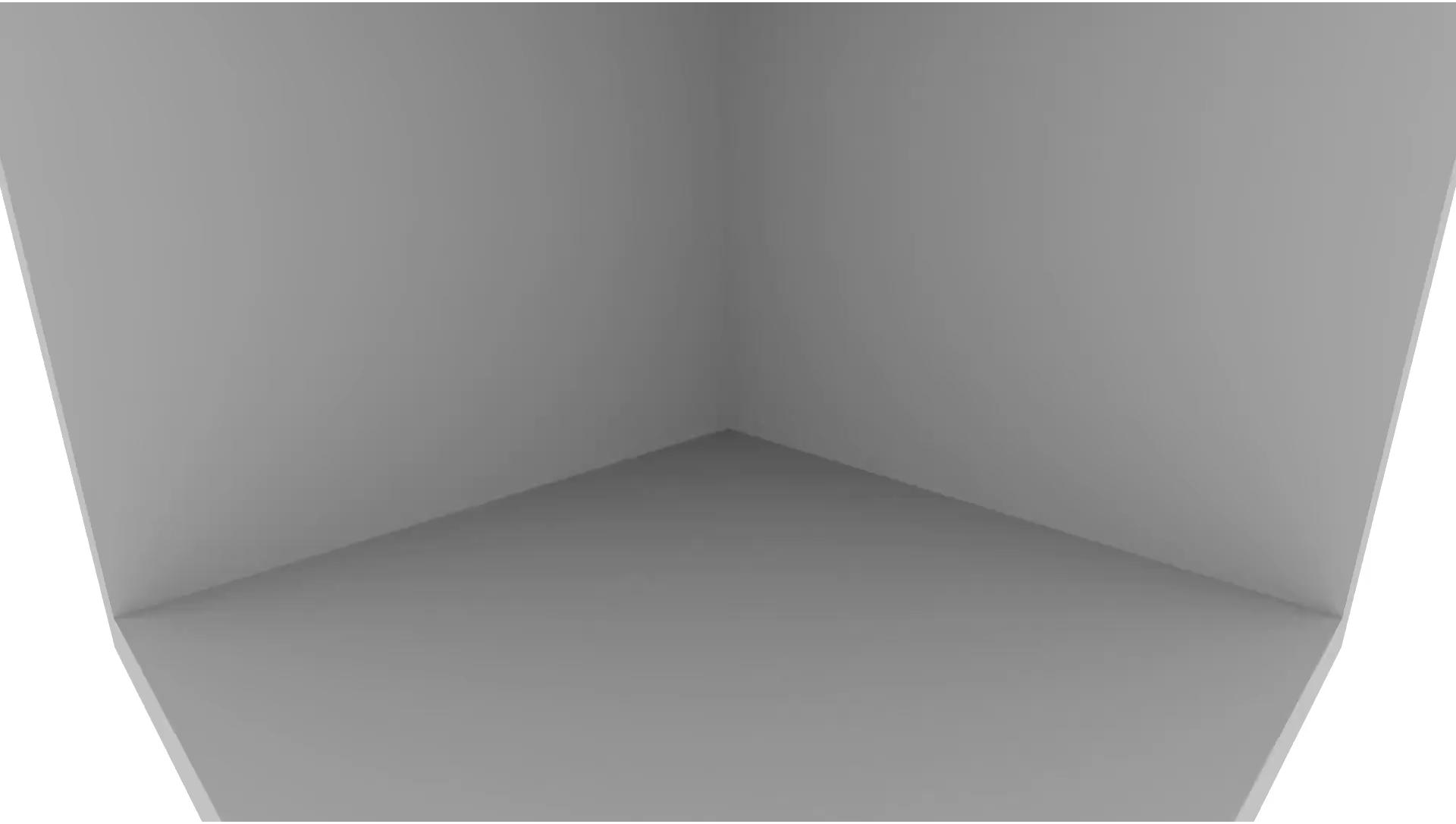
inclusion of elastic interaction (intrinsic or external) leads to spatial variations of T_c

- Magnetic inclusions for enhanced pinning

magnetic inclusions have long-range interaction
→ *could strongly suppress thermal creep*

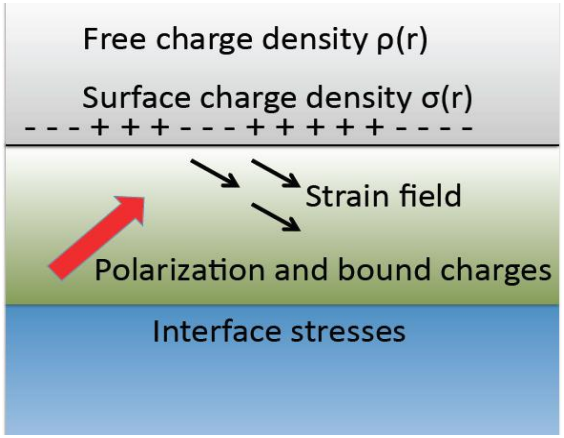
Large scale simulations of granular flows

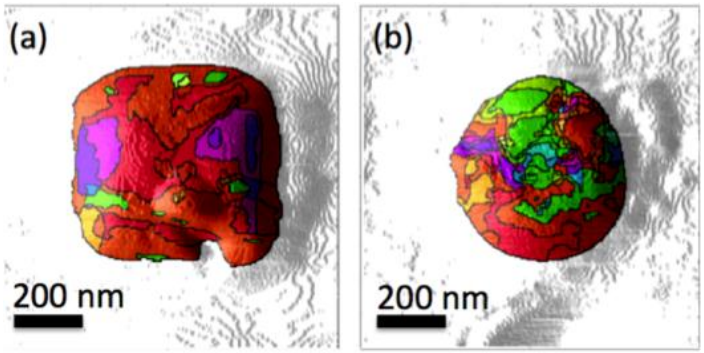




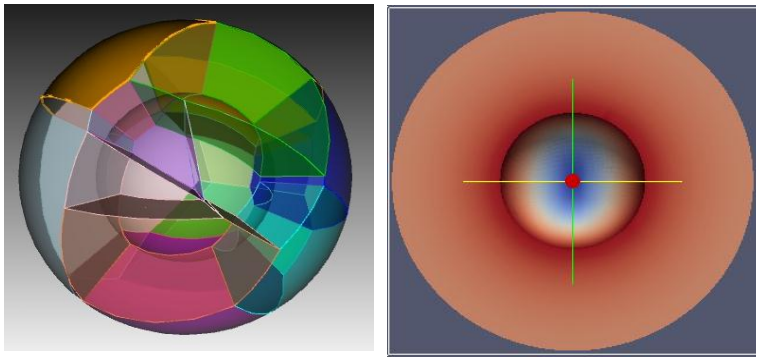
Coupled mesoscale problems

- Long-range strain fields – microstructural evolution in heterogeneous systems
  - Interfaces, surfaces – surface strain
  - Patterned systems
- Interactions with other order parameters
  - Ferroelectric polarization
  - Magnetization density
  - Free charges





Ferroelectric domains in $BiFeO_3$ patterned structures (S. Hong et al.)

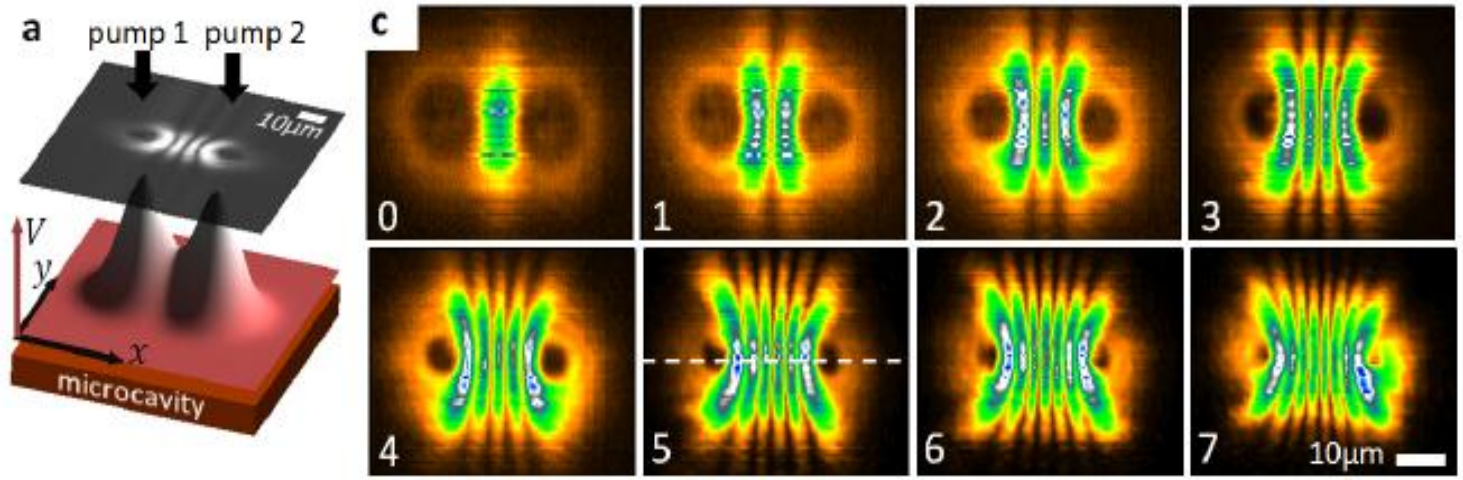


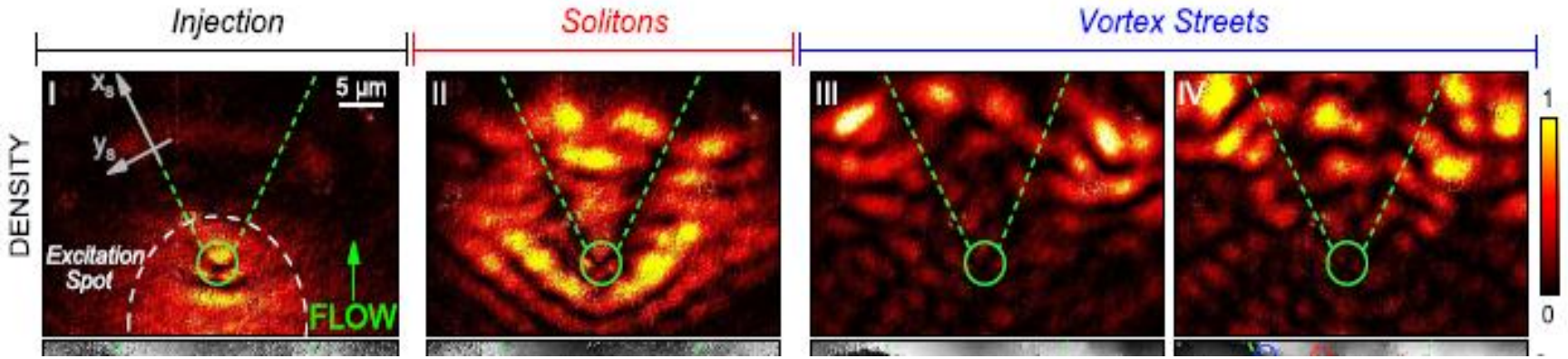
Stress in a core-shell nanoparticle

- Goal: scalable computational methods for microstructural evolution of strongly-coupled mesoscale problems

Nonlinear dynamics of quantum condensates

Tosi et al Nature Physics 2012





Grosso et al 2011

Status

- Individual tools being driven to a high level in specific application areas
- Integration across scales still a problem
  - Particularly for concurrent methods
  - Parameter passing still the rule
- “Data-driven” methods growing
  - Model discovery in its infancy but promising
  - Trees not genomes
  - Concurrent simulation/experiment a goal
- Changing computer architectures
  - Progress driven by algorithm development on earlier generation machines
  - New machines need to solve new problems

What would we like to be able to do

- Accuracy: complex multi-atomic structures with energy scales ~ $k_B T$
- Excitations: multiply excited electronic states in complex solids, fluids, and interfaces
- Embedding: solving each piece of the problem at the appropriate level of accuracy
- Sampling: fast smart searches in configuration space

Accuracy

Only quantum chemical methods have the required accuracy to model thermal effects, water, etc. (and then only in the ground state)

These will never work on large systems

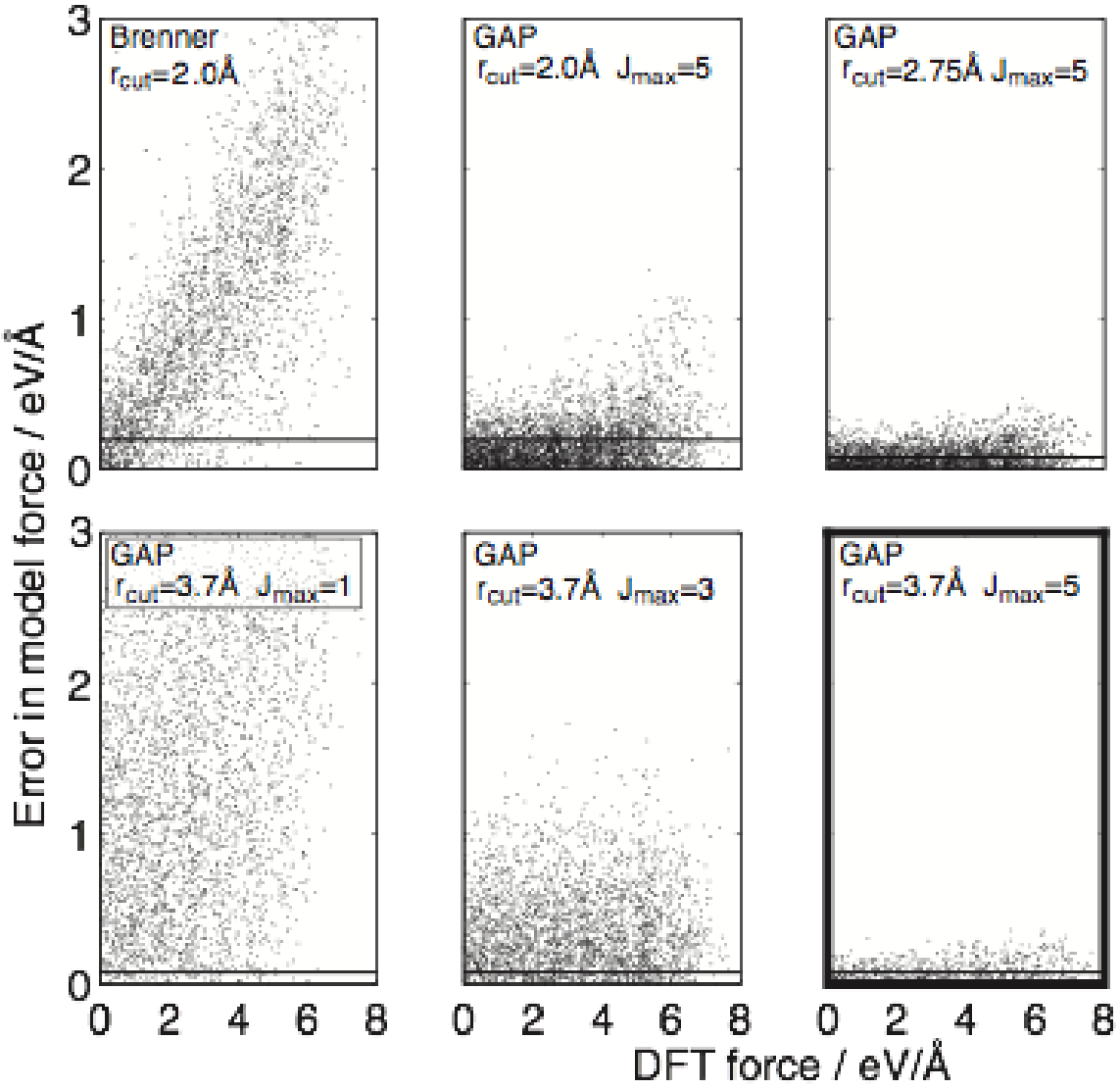
Can we invent “principled” force field methods

Assume that you can do arbitrarily accurate QM calculations *but very infrequently* and “fit” them to force fields

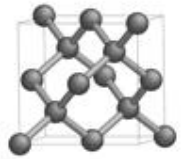
Two major issues: basis functions; fitting procedure

Turn the computational problem into a “big data” problem

Force correlation with QM



Diamond
(1000 K)

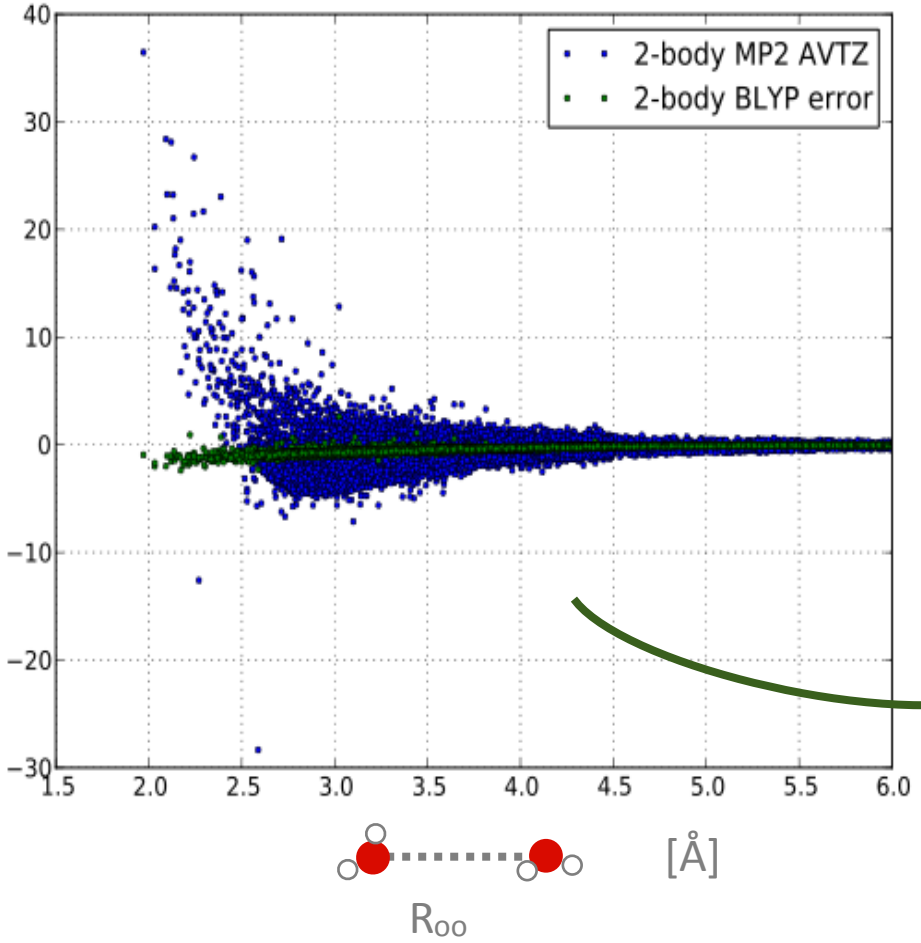


Theoretical limit
for given cutoff:
RMS of
long range forces

Energy error < 1 meV (0.02 kcal/mol) / atom

H_2O dimer interaction energy: MP2 AVTZ

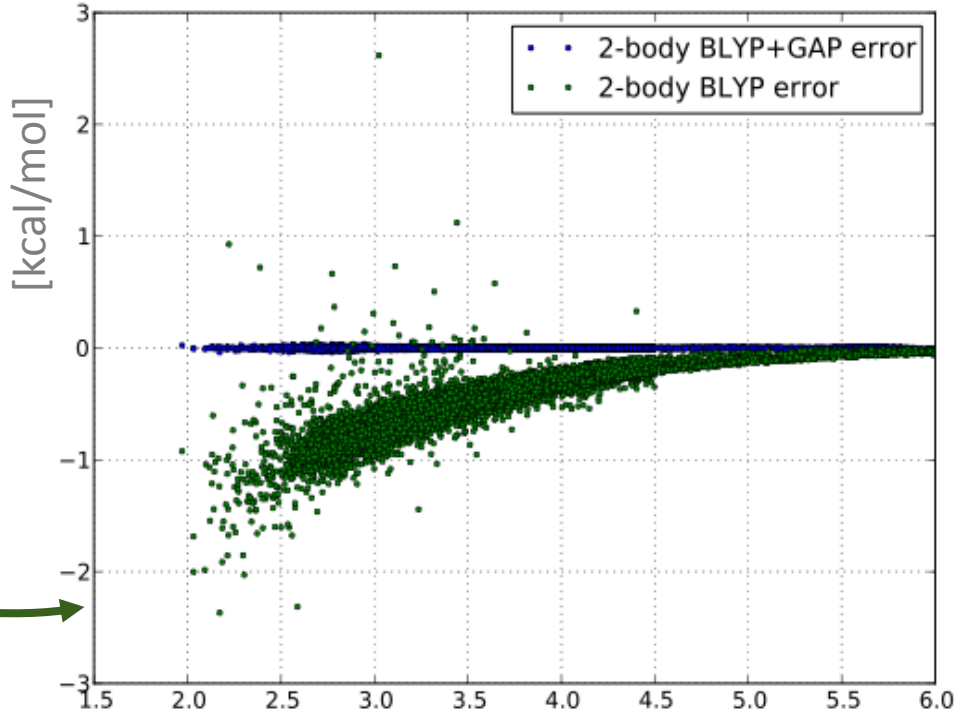
BLYP error



[Å]

R_{OO}

(BLYP+GAP) error



[Å]

R_{OO}

~ 80% of the interaction energy: 0.55 RMS

~99.8% of the interaction energy: 0.006 RMS

Excitations

Density functional theory applies only to the ground state

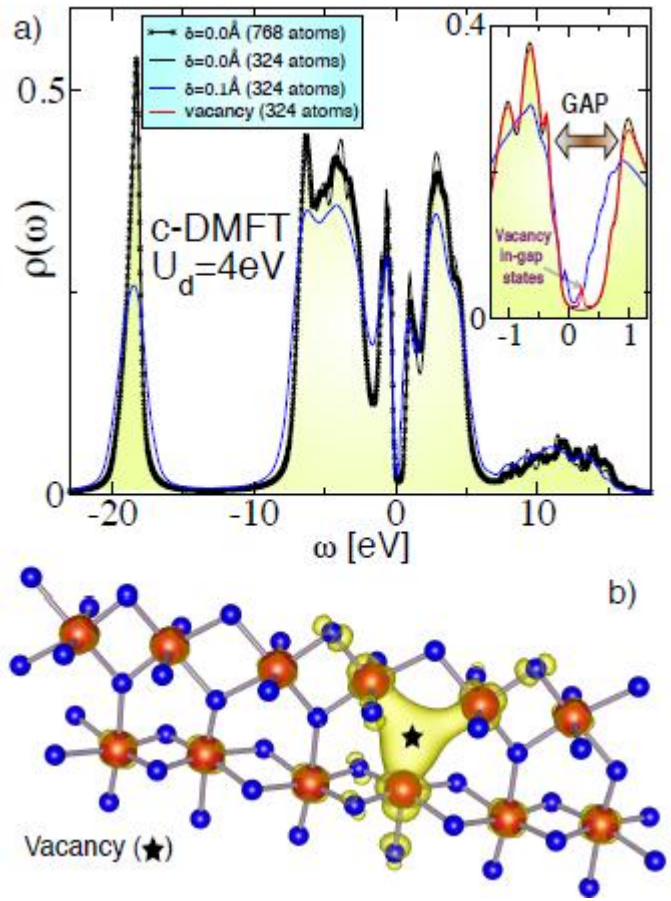
Energy gaps in semiconductors typically wrong by factor of 2 or more

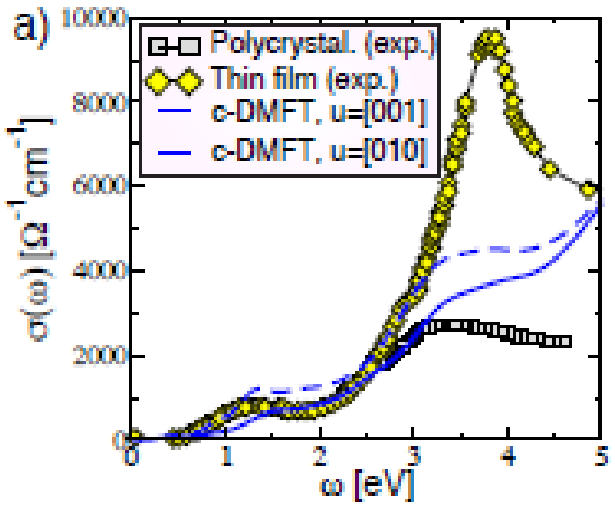
No decent treatment of correlation effects: magnetism, Mott physics, excitons, superconductivity, ferroelectricity, ...

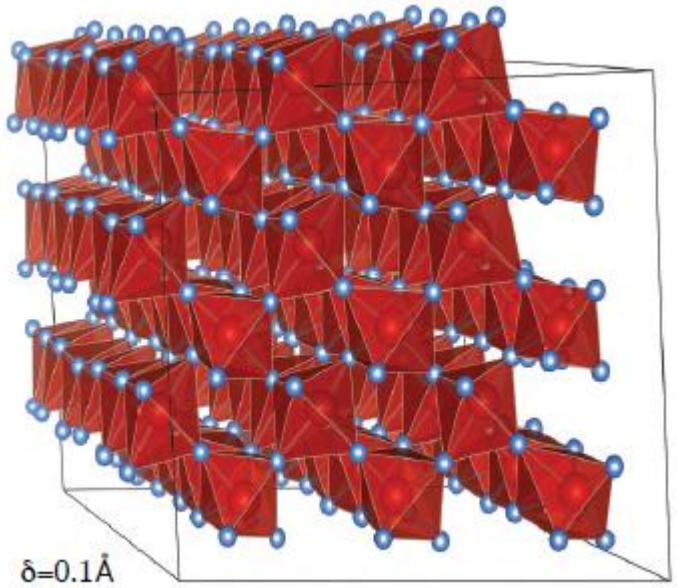
Even quantum chemical methods are usually unrewarding: … but

- *Initiator*- Full Configuration Interaction Quantum Monte Carlo (i -FCIQMC)
- Cluster-Dynamical Mean Field Theory
- Effective Hamiltonians - reduced basis state methods
- Density Matrix Embedding

Cluster-dynamical mean field theory on VO_2







Weber et al. PRL 2012

Sampling

LDFT calculations on large systems are now free

Variational QMC calculations will soon be so

Interesting directions in MC-CI

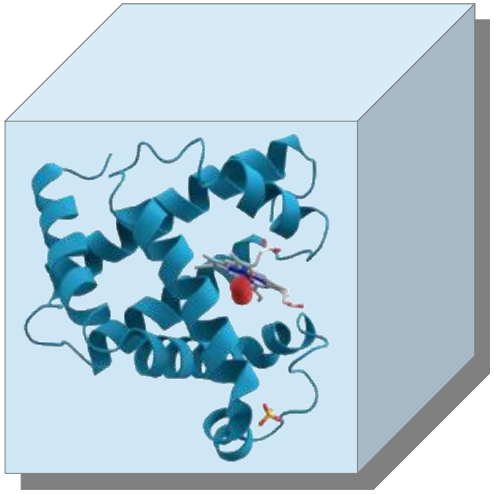
Large-scale structure searches are now routine

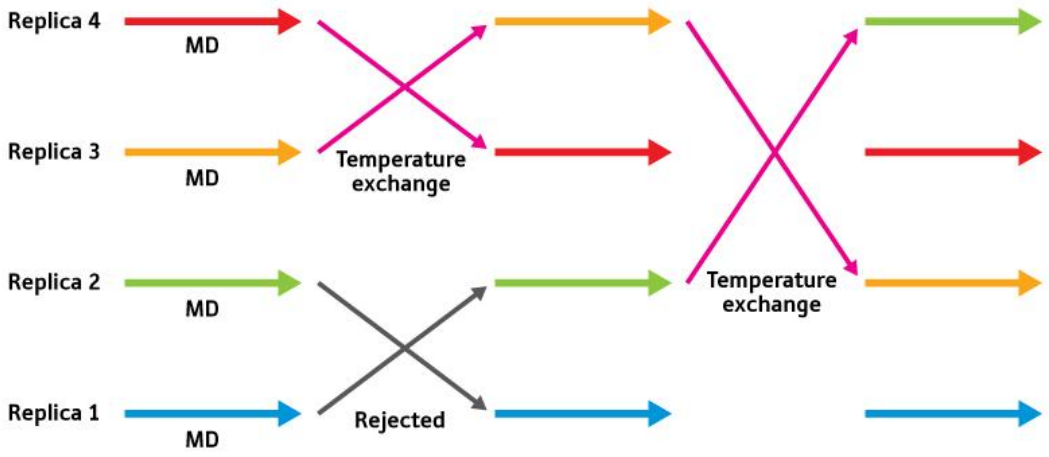
Timescale problem for slow dynamics and rare events

… this is generating a lot of data ….

Ensemble Molecular Simulations

Challenge: Single molecular dynamics (MD) trajectories cannot capture long timescales, especially rare events and thermodynamics.





Methods:

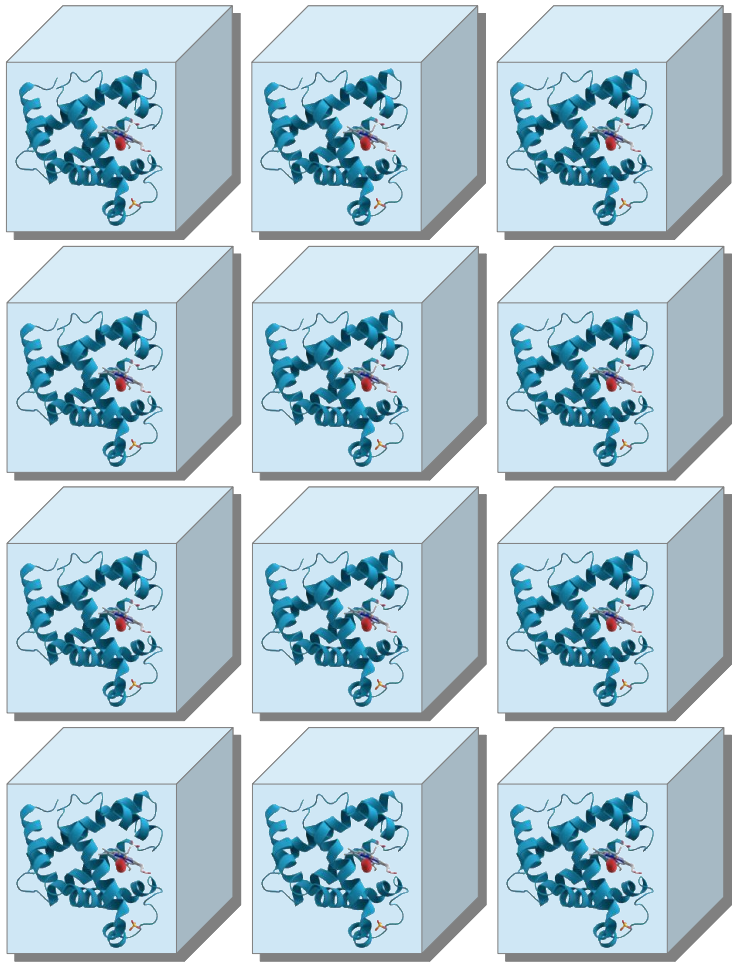
- Replicate Exchange (RE)
- Umbrella Sampling (US)
- Hybrids (REUS), etc.

Implementation goals:

- New methods, applications should be easy for the scientist
- Exploit peta/exascale machines

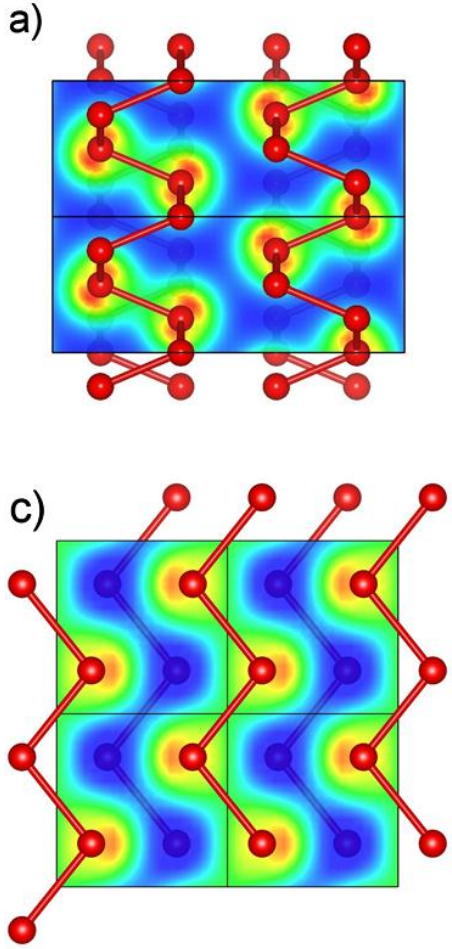
Ensemble Molecular Simulations

- UC-ANL SCI (Hammond/Dinner) developed nonequilibrium umbrella sampling (NEUS), which is communication-intensive, for BG/P, Cray using Global Arrays [1].
- Recognized the need for more general molecular dynamics capability and friendly environment for domain scientists to develop new algorithms.
- New LAMMPS-Ensembles software that implements RE, US, Plumed [2] using LAMMPS library interface (black box, if so desired). Will scale to all of BG/Q.



[1] *J. Chem. Theory Comp.* **7**, 2710 (2011)
[2] http://www.plumed-code.org/

Structure searches

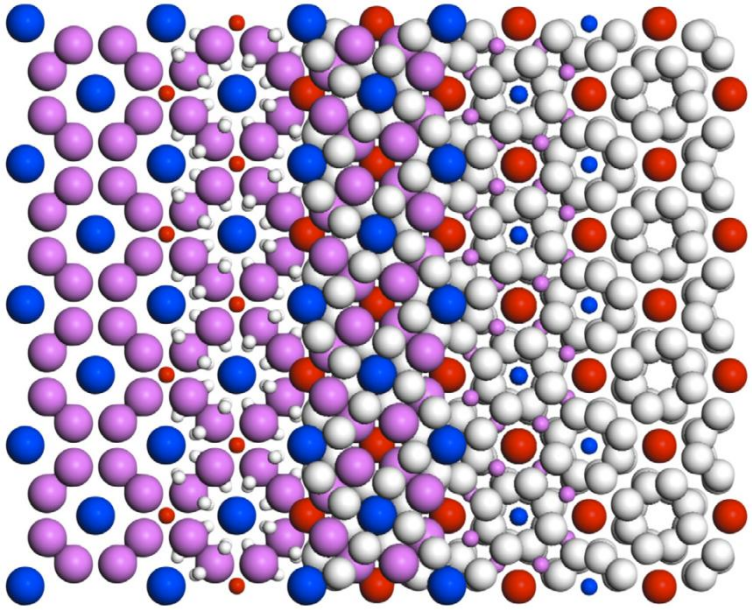


Polymeric Oxygen at High Pressures

Sun et al., PRL 108, 045503 (2012)

Ba-IV and Rb-IV host-guest structures

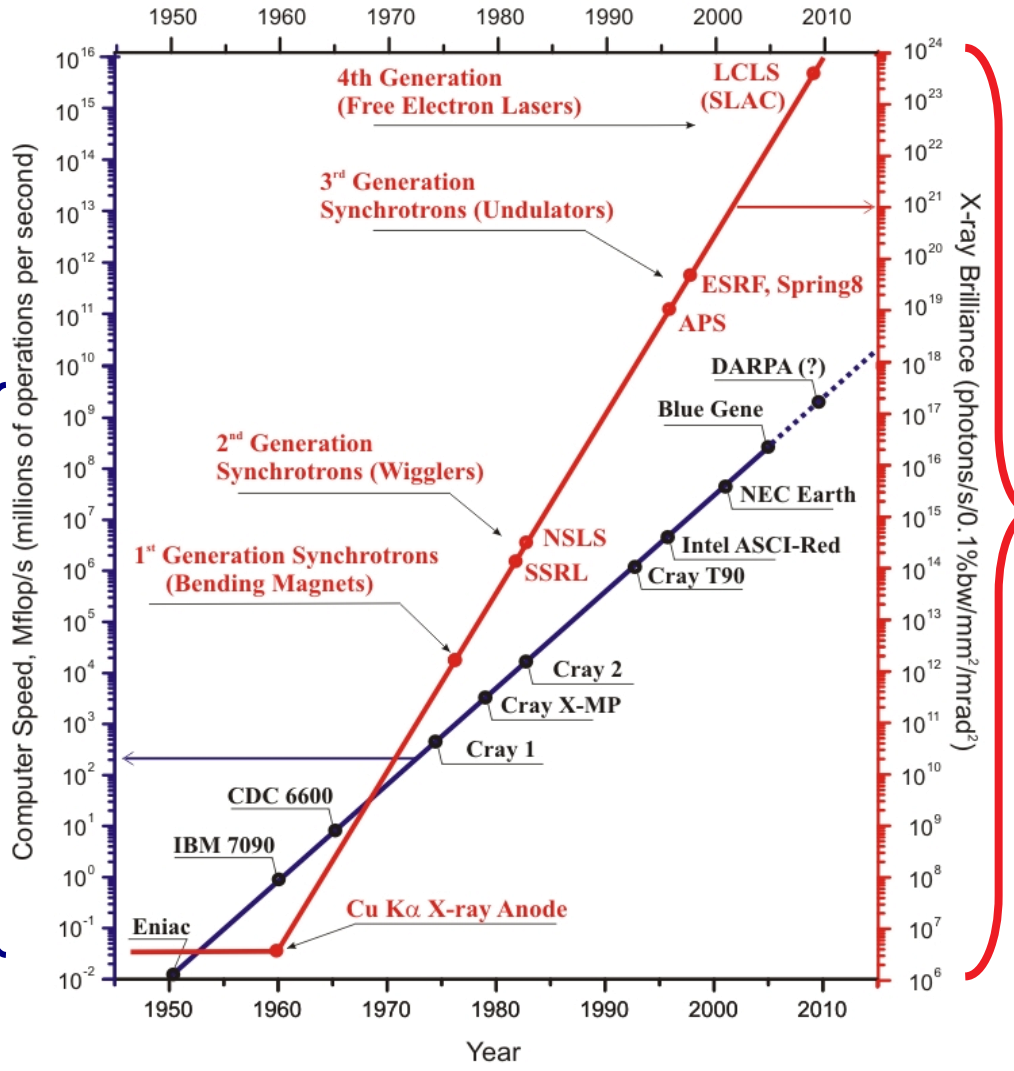
Pickard and Needs, J. Phys.: Condens. Matter **23** (2011) 053201



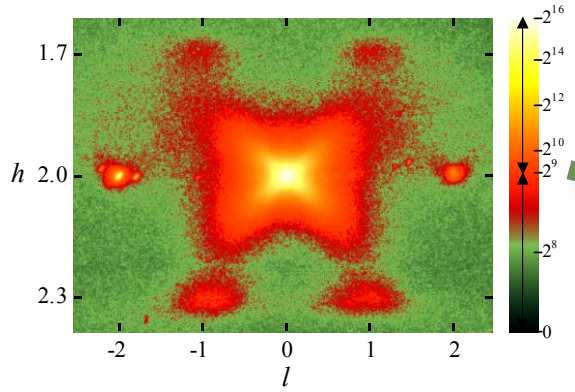
“Big data”

- Volume: e.g. sky surveys, computational structure
- Velocity: e.g. 4D detectors in X-ray, neutron scattering
- Variety: biology, materials science, chemistry,

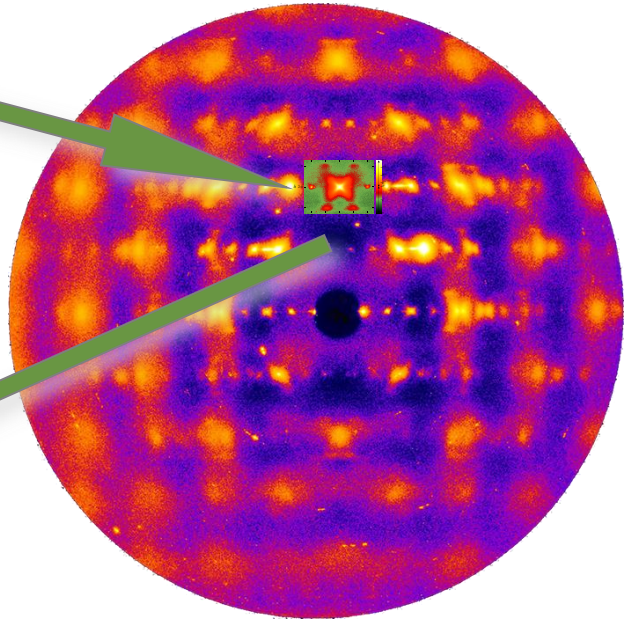
Computers: 12 orders of magnitude in 6 decades



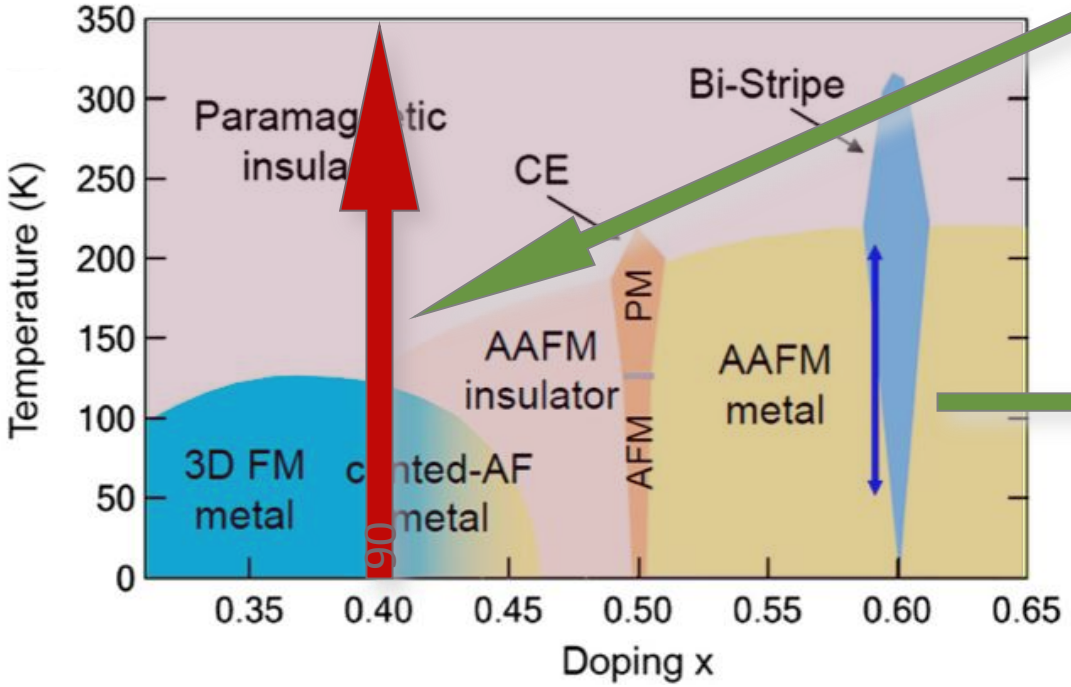
Light sources: 18 orders of magnitude in 5 decades



Total Data: S(Q, T, x)



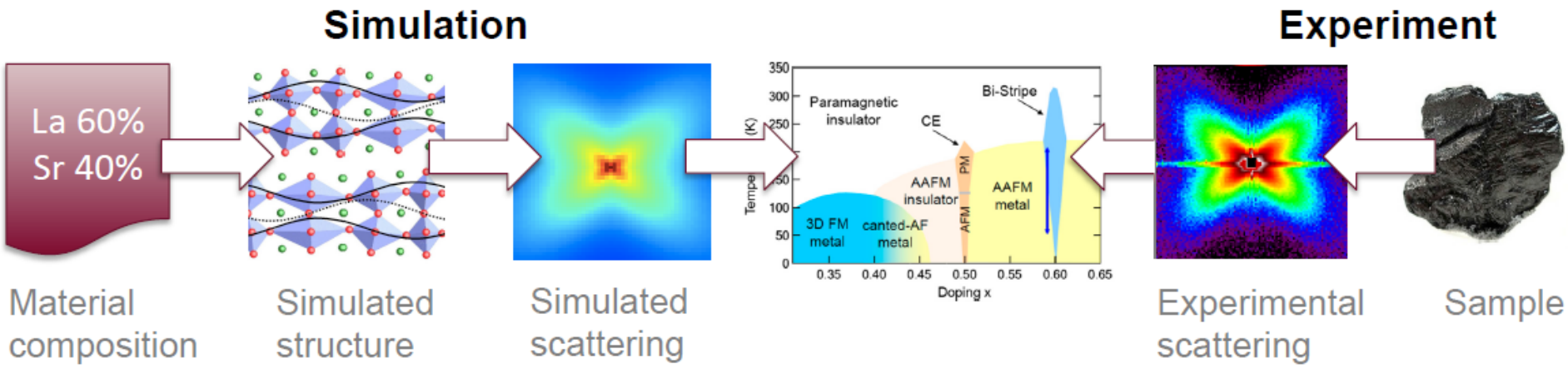
Phase Diagram of Bilayer Manganites



Correlated Data Analysis/ Machine Learning

Materials science example: Diffuse scattering

"Most of materials science is bottlenecked by disordered structures"



Use experiments to constrain models of material structure, and vice versa

- Experiments: Single crystal diffuse scattering of, e.g., bilayer manganites, yielding pair distribution functions
- Simulations: Molecular dynamics for candidate structures, yielding simulated scattering and simulated pair distribution functions

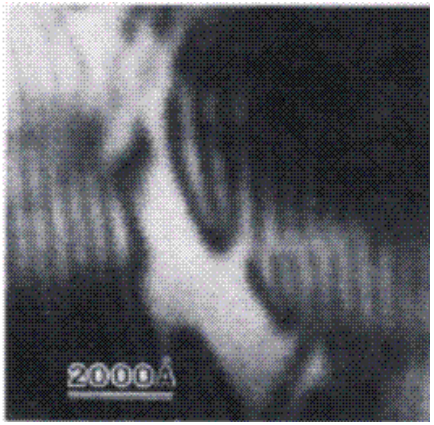
- Automated workflows for data reduction
- Visualization: parallel scripting for large data volumes
- Real time data analysis and visualization tools
- Petascale active data storage
- Real time data simulations
- Model optimization and (automated) parameter extraction
- Data cataloguing and retrieval

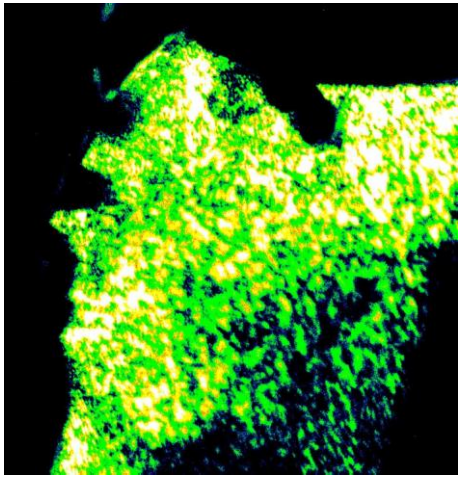
Soft Electronic Matter

Modulated electronic phases

- Charge and spin density waves have been known for many decades – in “strongly correlated” systems they are the rule not an exception
- Added: nematics, multiferroics,

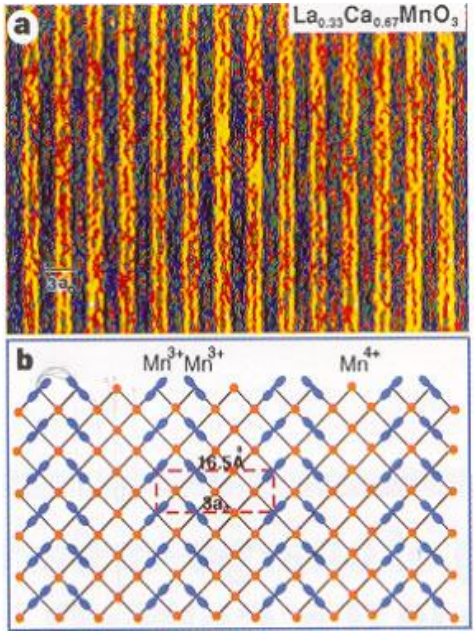
$TaSe_2$: Chen 1984



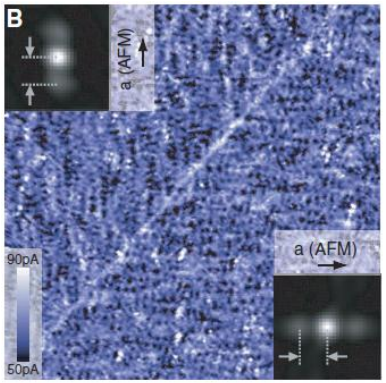


100 nm

Charge-order in $LaCaMnO_3$
Loudon & Midgley 2005



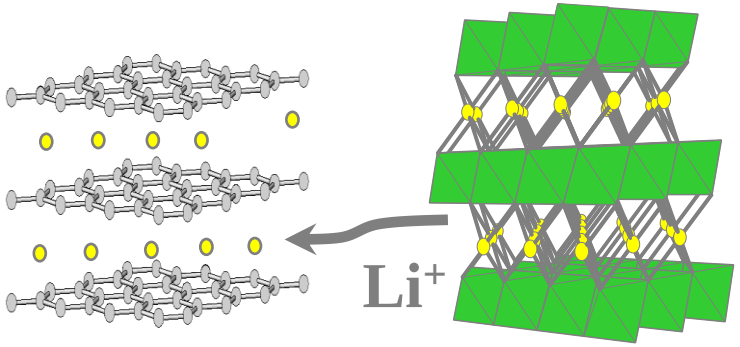
S Mori et al 1998



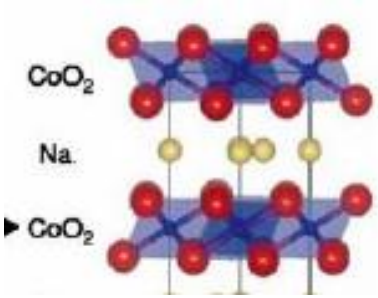
FeAs: Chuang et al Science 2010

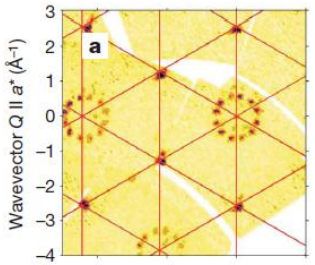
Energy dense materials are strongly correlated

Li-ion battery, commercialised by Sony in 1991
$Li_x C_6$ (anode) / $Li_{1-x} CoO_2$ (cathode)
x limited to ~ 0.5



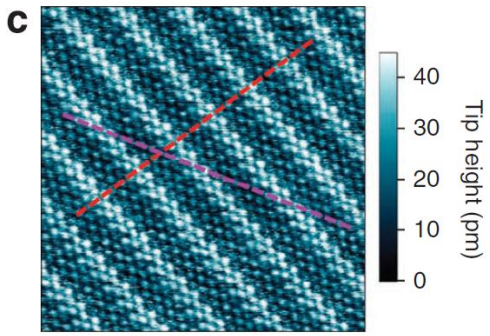
$Na_x CoO_2$
Enhanced thermopower, 5K superconductor
vacancy ordered phases

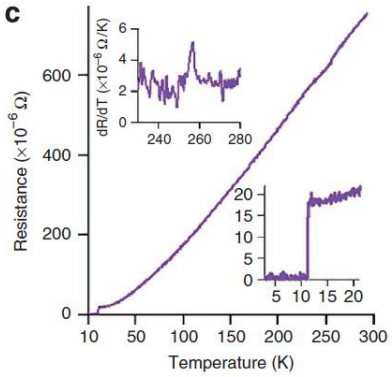




Roger et al. 2007 doi:10.1038/nature05531

CaC_6
12K superconductor; 250K CDW

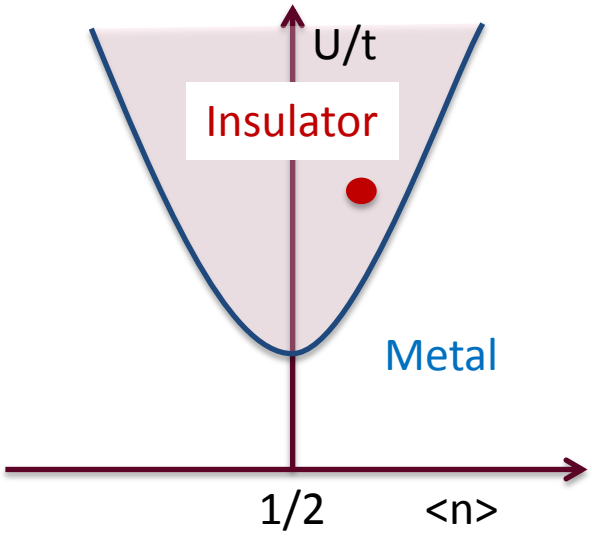


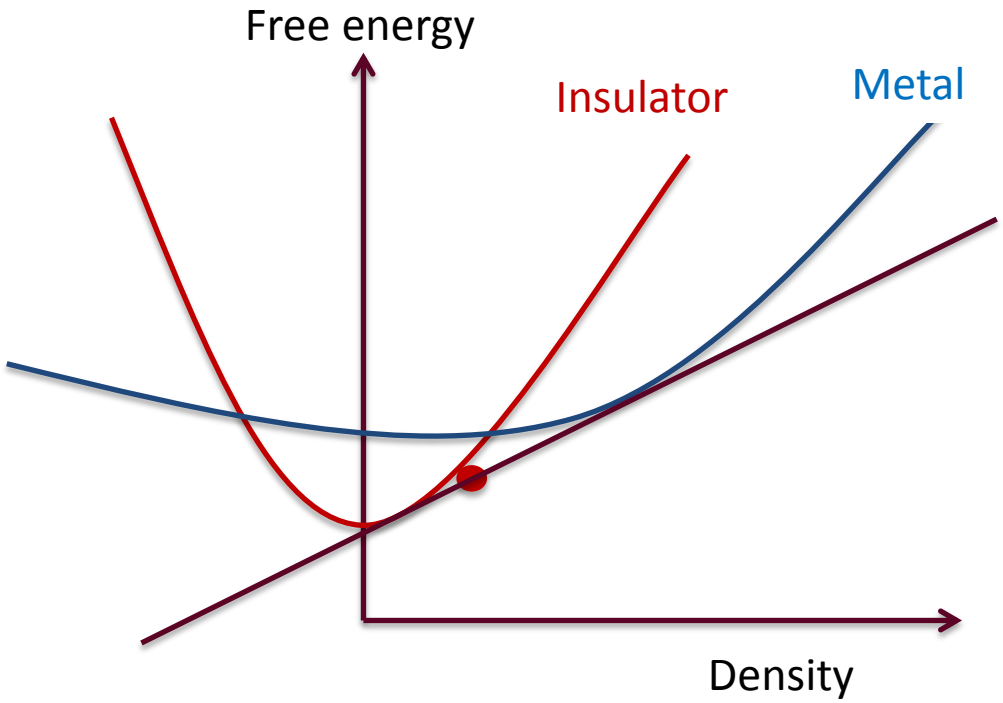


This is not an accident!

Rahnejat et al 2011 DOI: 10.1038/ncomms1574

Doping of a Mott insulator

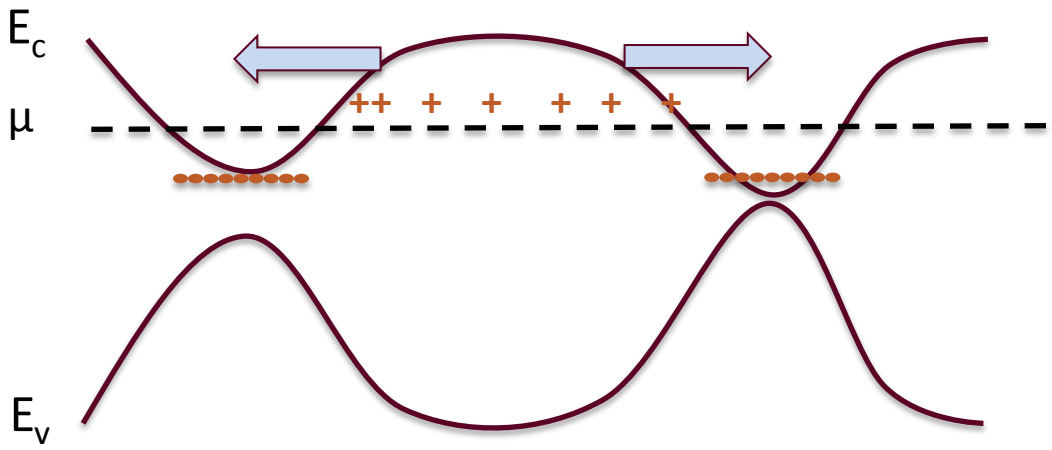




Expect phase separation and an inhomogeneous state
"Frustrated" by Coulomb interaction

Inhomogeneous phases in Mott systems

Mobile donors diffuse to form metallic puddles and screen Coulomb repulsion of phase-separating carriers

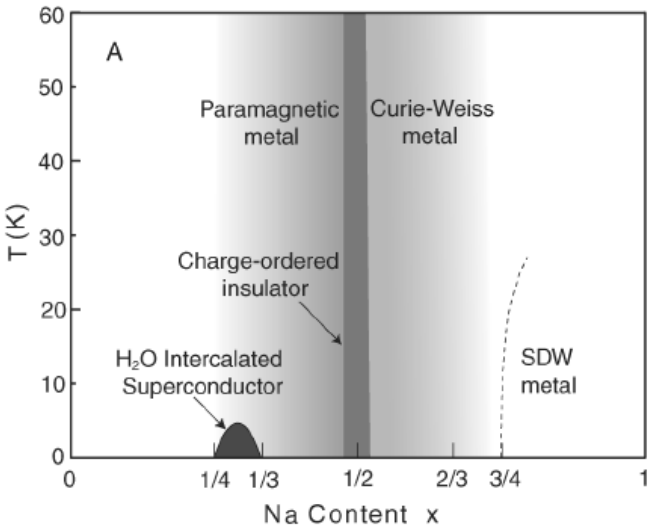


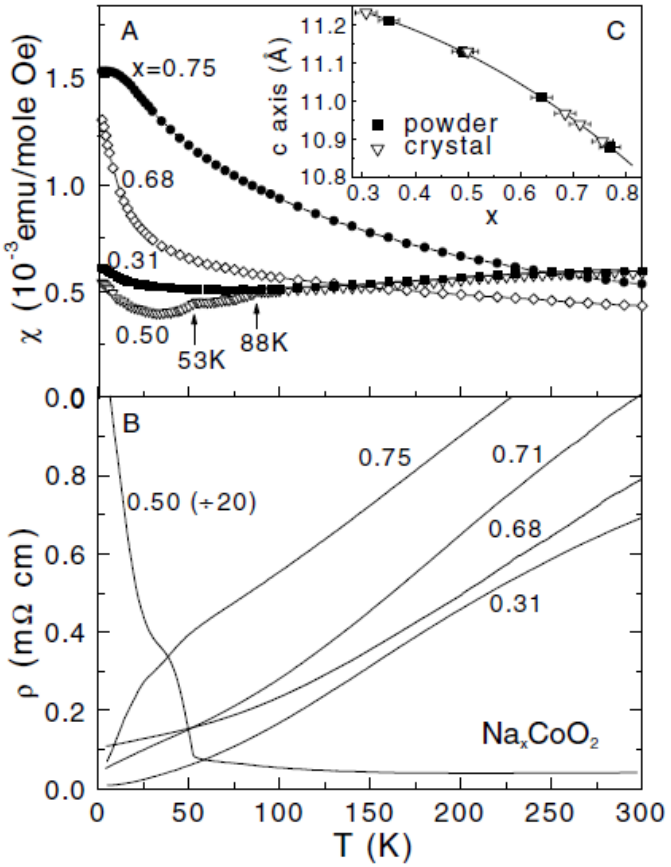
This is a generic feature of any system with a first-order phase transitions separating stable phases of differing electron density

Particularly prevalent when dopant species are highly mobile – e.g. O vacancies and Li ions

Charge Ordering, Commensurability, and Metallicity in the Phase Diagram of the Layered Na_xCoO_2

Maw Lin Foo,[1] Yayu Wang,[2] Satoshi Watauchi,[1,*] H.W. Zandbergen,[3,4] Tao He,[5] R. J. Cava,[1,3] and N. P. Ong[2,3]

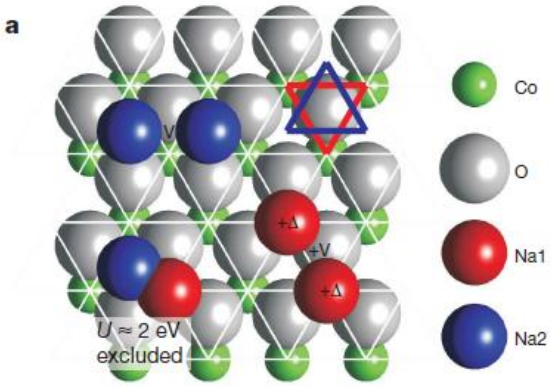


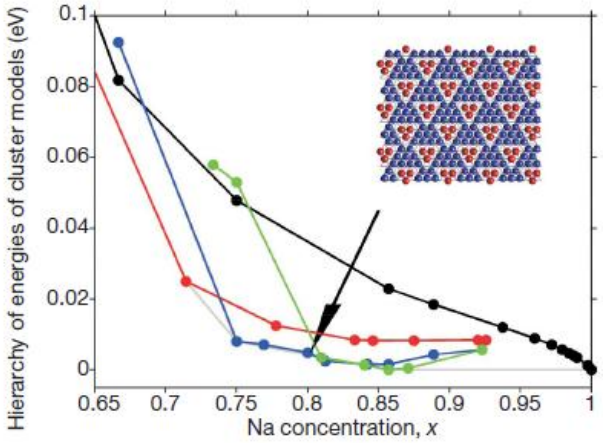


Patterning of sodium ions and the control of electrons in sodium cobaltate

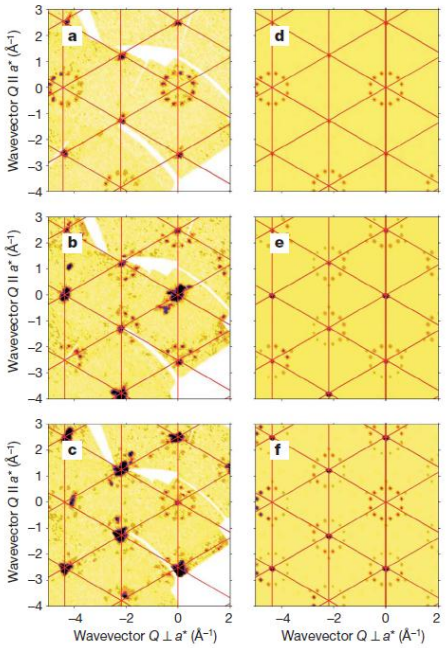
Vol 445 | 8 February 2007 | doi:10.1038/nature05531

M. Roger[1], D. J. P. Morris[2], D. A. Tennant[3,4], M. J. Gutmann[5], J. P. Goff[2], J.-U. Hoffmann[3], R. Feyerherm[3], E. Dudzik[3], D. Prabhakaran[6], A. T. Boothroyd[6], N. Shannon[7], B. Lake[3,4] & P. P. Deen[8]





Ordered trivacancy phase of $Na_{0.8}CoO_2$

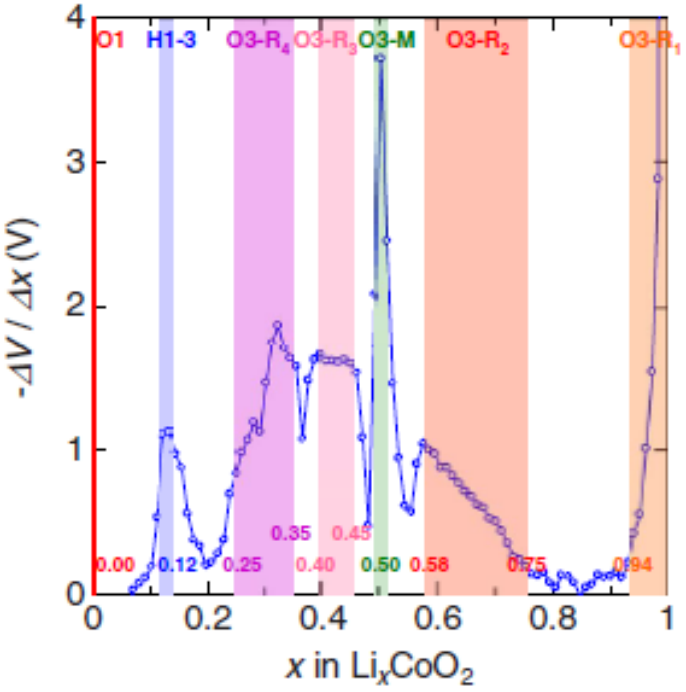


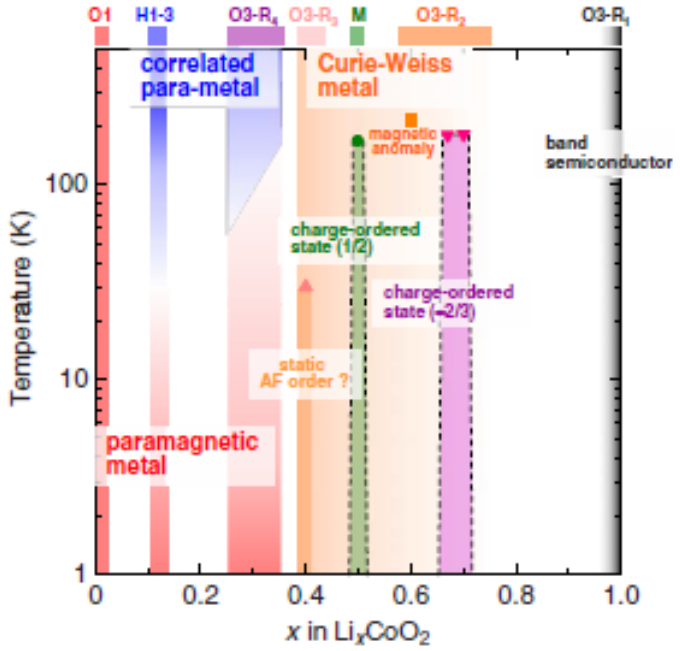
PHYSICAL REVIEW B 80, 165114 (2009)

Electronic phase diagram of the layered cobalt oxide system Li_xCoO_2 $(0.0 \leq x \leq 1.0)$

T. Motohashi,[1,2] T. Ono,[2,3] Y. Sugimoto,[1] Y. Masubuchi,[1] S. Kikkawa,[1] R. Kanno,[3] M. Karppinen,[2,4] and H. Yamauchi[2,3,4]

Derivative of open cell voltage dV/dx indicates biphasic regions

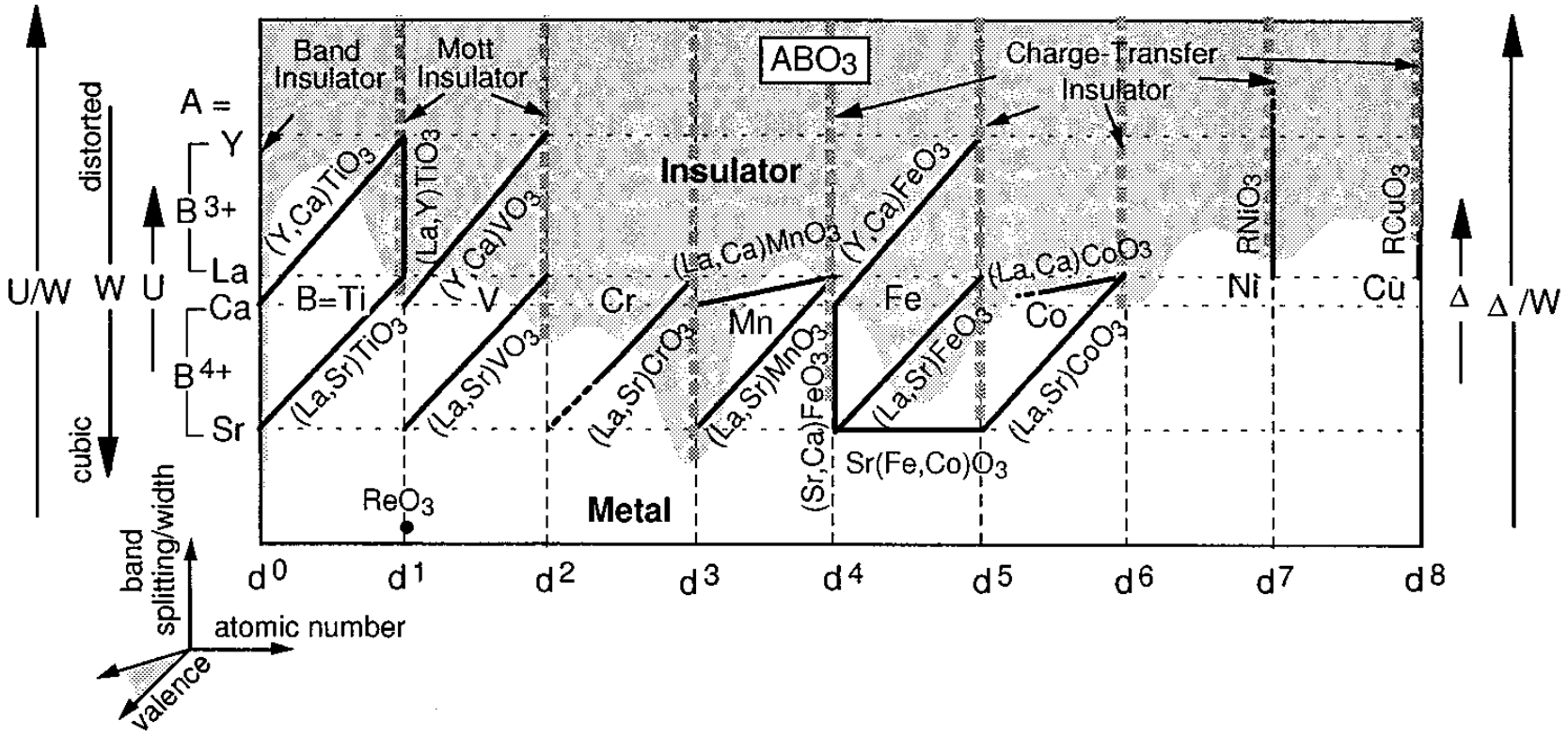




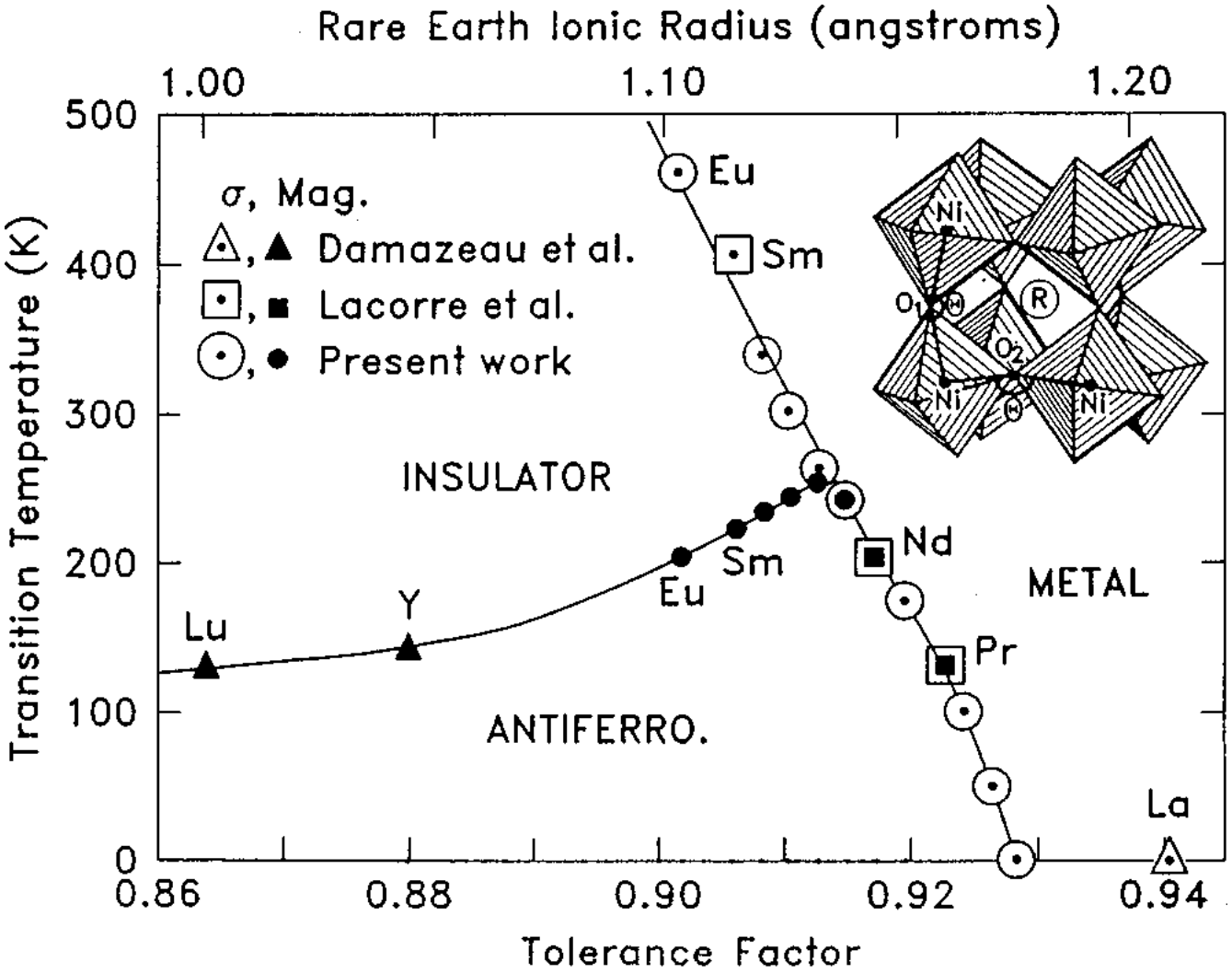
Mitigation

- Explicit multiphase mixture with rigid backbone stuctures
- “Jamming” and size-control

Metal-Insulator transitions in perovskite 3d oxides

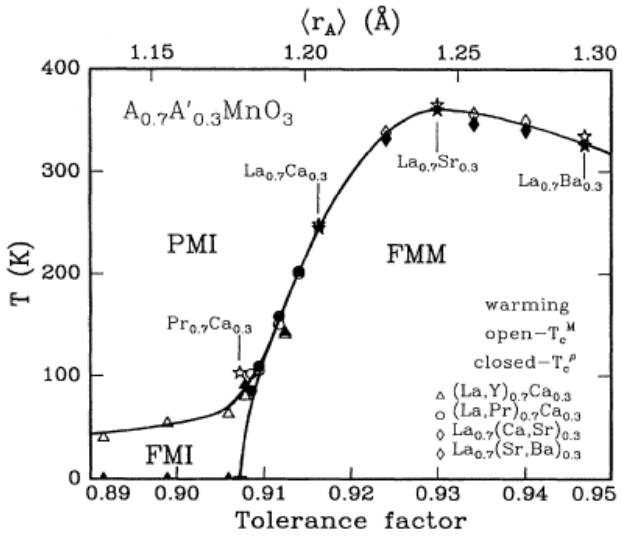


A schematic metal-insulator diagram for the filling-control (FC) and bandwidth-control (BC) 3*d* transition-metal oxides with perovskite structure. From Fujimori, 1992.

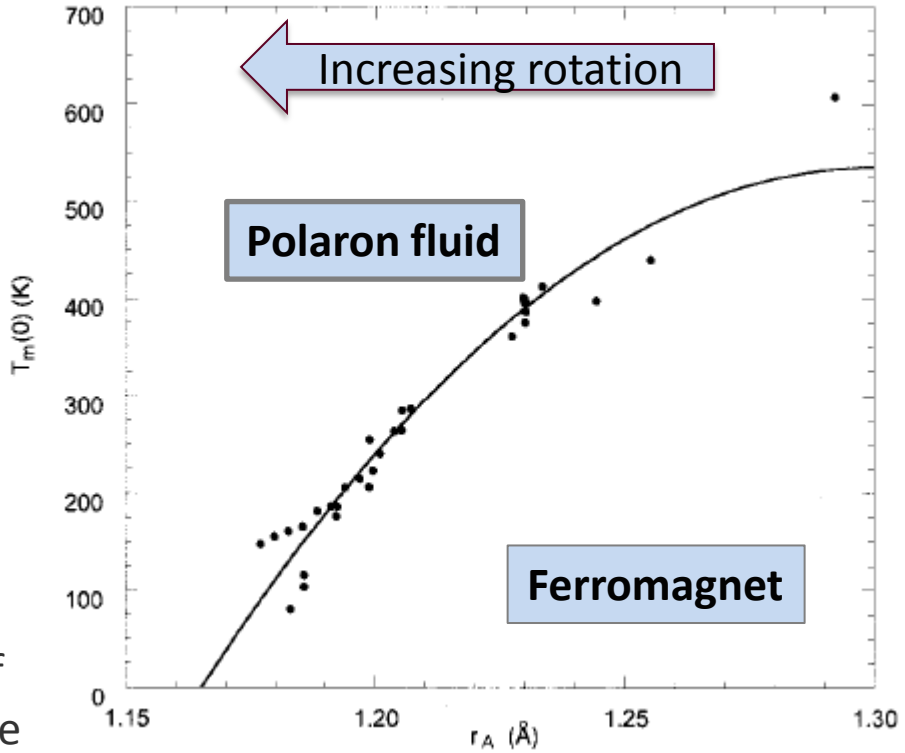


Electronic phase diagram of *R*NiO3 (Torrance *et al.*,1992).

Colossal magnetoresistance in manganites controlled by size of A-site cation



Hwang et al, PRL 75, 914 (95)

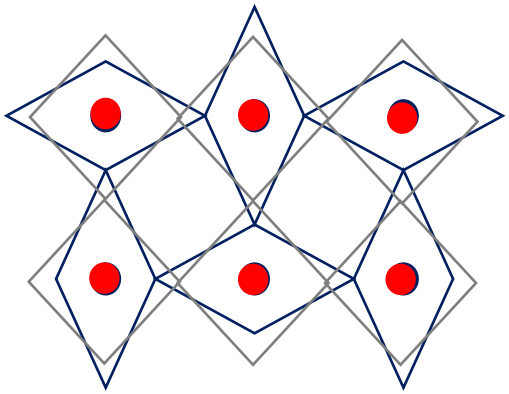


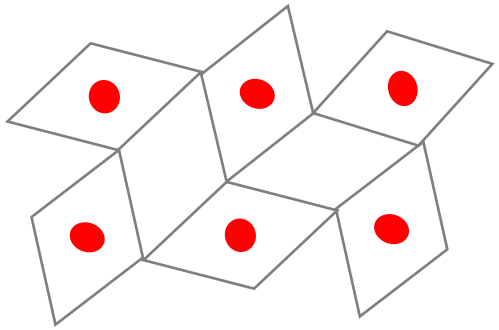
Rodriguez-Martinez and Attfield PRB 54 15622 (96)

Magnetic transition temperature of $Ln_{0.7}M_{0.3}MnO_3$ varying size of the A-site cation at fixed doping

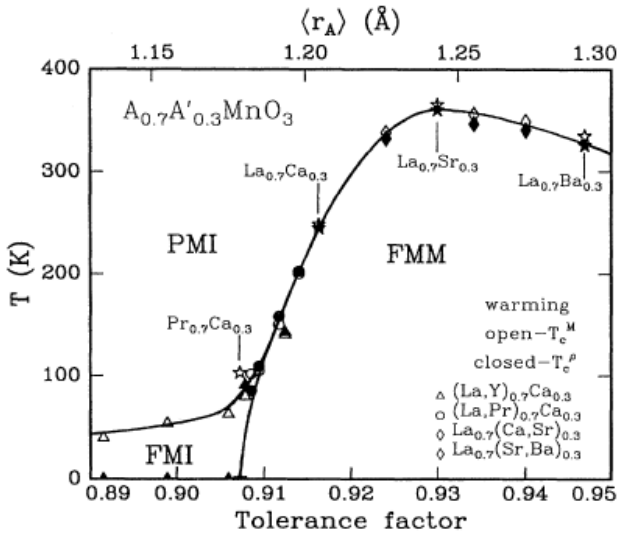
How do you make a polaron liquid?

- In a cubic system, a local J-T distortion propagates to infinity ... can this be screened?
- With rotations of octahedra inhomogeneous patterns are allowed

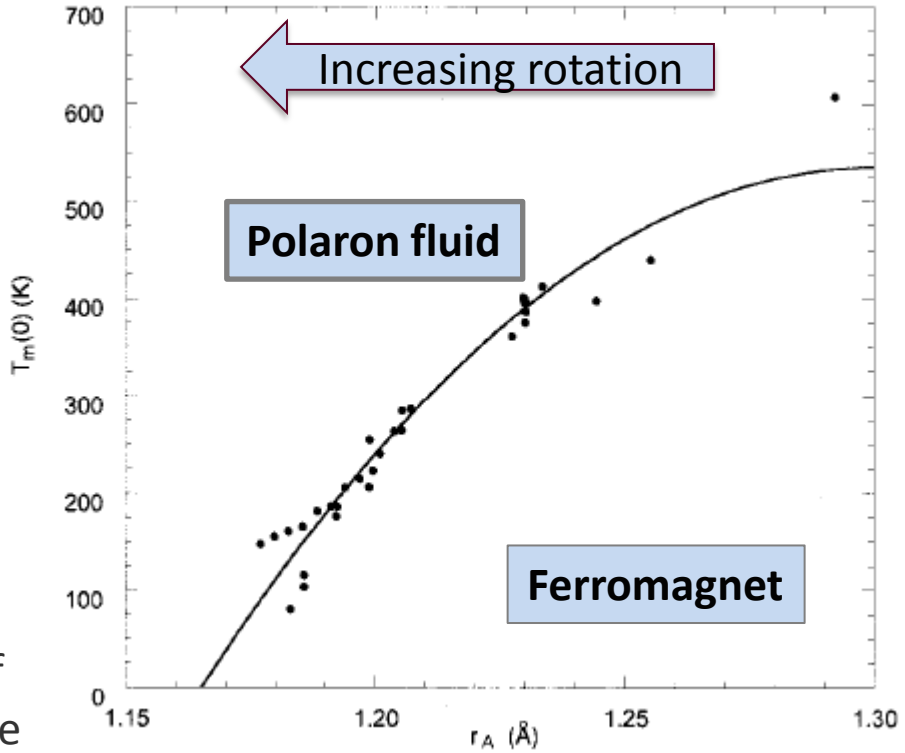




Colossal magnetoresistance in manganites controlled by size of A-site cation



Hwang et al, PRL 75, 914 (95)



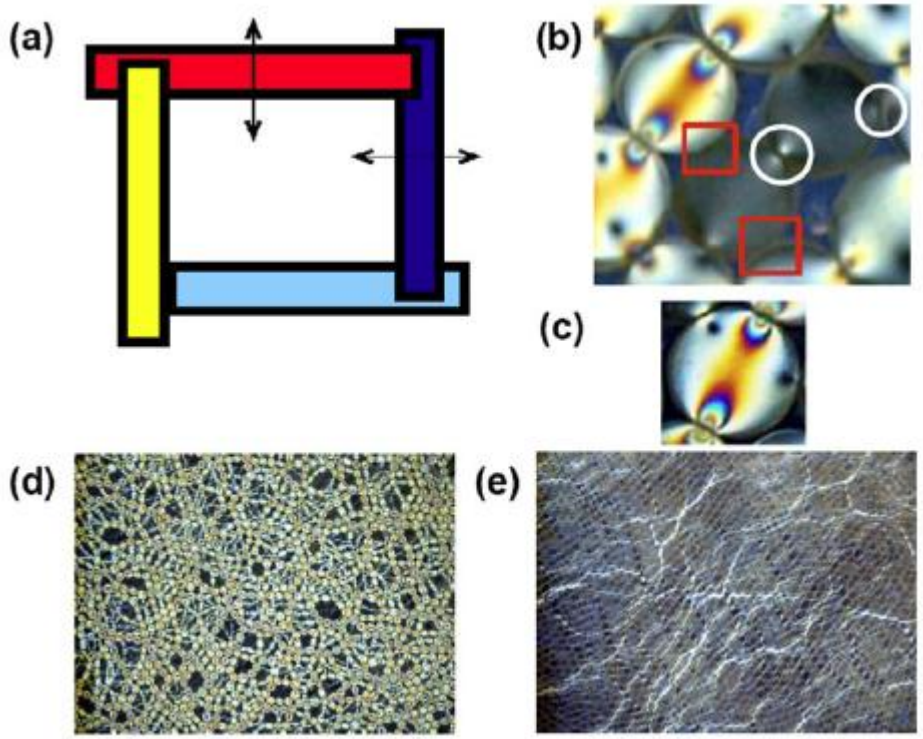
Rodriguez-Martinez and Attfield PRB 54 15622 (96)

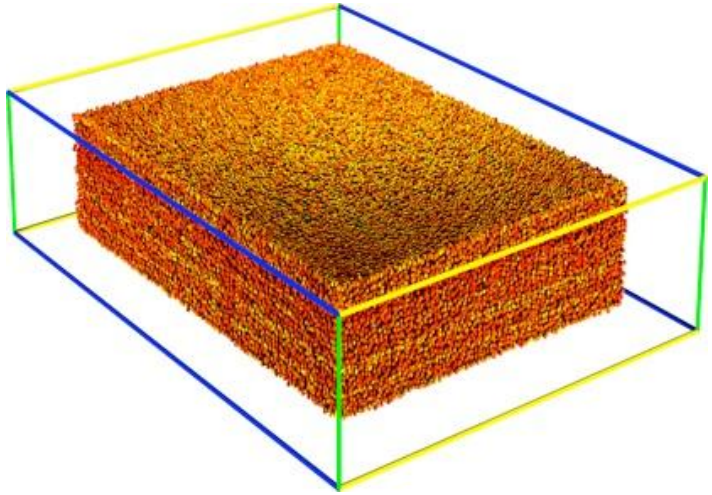
Magnetic transition temperature of $Ln_{0.7}M_{0.3}MnO_3$ varying size of the A-site cation at fixed doping

Jamming Transition in Granular Systems

T. S. Majmudar,[1] M. Sperl,[1] S. Luding,[2] and R. P. Behringer[1]

PRL **98,** 058001 (2007)





3D reconstruction of ~10M pNIPAM colloids (Nagel group)

Outlook

Are there systematic ways to make structurally (and electronically) “soft” phases in oxides, for example

- negative thermal expansion materials
- fragile glasses
- polaronic liquids, nematics, smectics, ...
- electrocaloric materials
- low coercivity ferroelectrics
- phase change materials
- strong quantum fluctuations near critical points and high T_c conventional superconductors
- ...