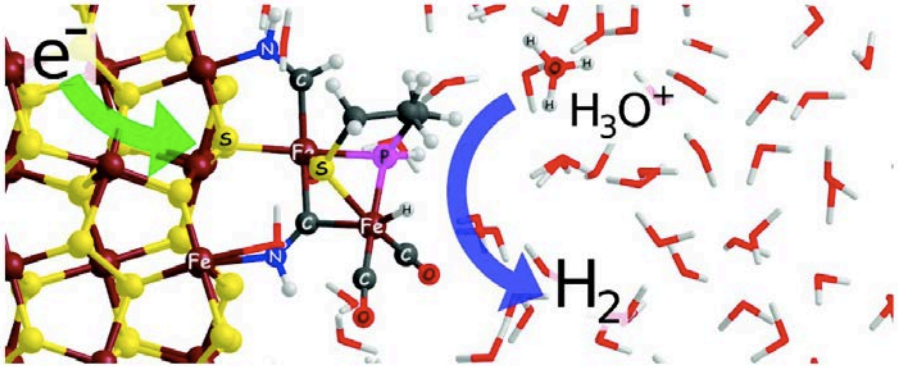
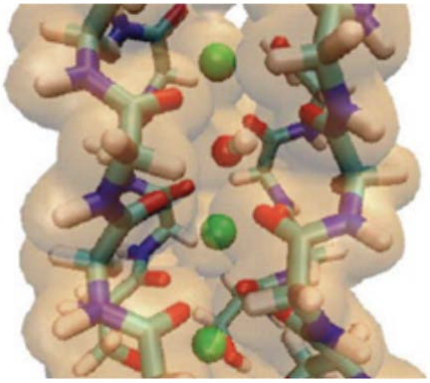
DOE SciDAC

2014 SciDAC-3 Principal Investigator Meeting, Washington DC, July 30 - August 1, 2014

Advanced Modeling of Ions in Solutions, on Surfaces, and in Biological Environments

http://amis-scidac.org/





The AMIS team

Roberto Car: Professor of Chemistry and Physics, Princeton
Weinan E: Professor of Applied Mathematics, Princeton
Michael L. Klein: Professor of Chemistry, Physics, and Biology, Temple
Lin Lin, Assistant Professor of Applied Mathematics, UC Berkeley
Esmond Ng, Senior Scientist, FASTMath, LBNL
Xifan Wu: Assistant Professor of Physics, Temple
Chao Yang, LBNL: Staff Scientist, FASTMath, LBNL

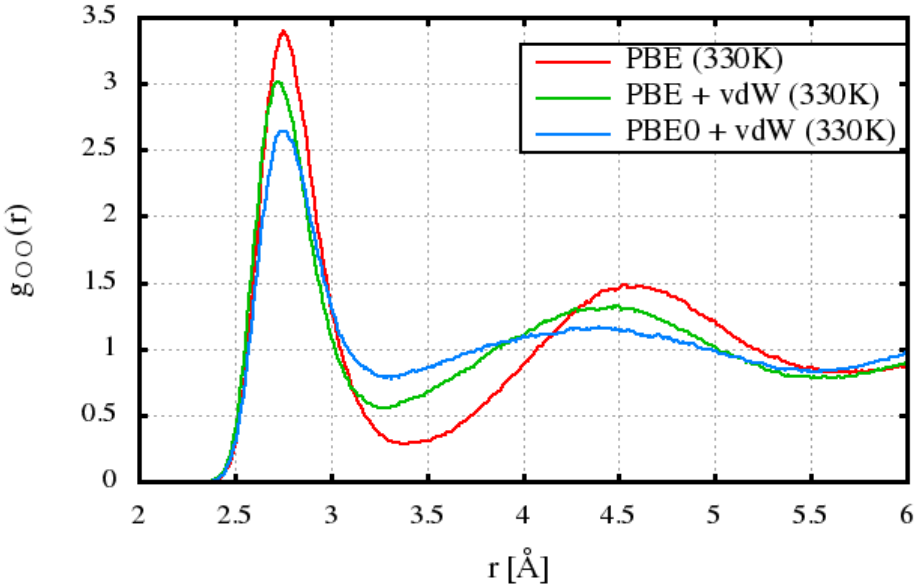
SIZE, TIME (SAMPLING), ACCURACY are all very important issues in molecular simulations

(from *Concluding Remarks @ 2013 PI meeting*)

- **ACCURACY**
- **SIZE**
- **TIME (SAMPLING)**

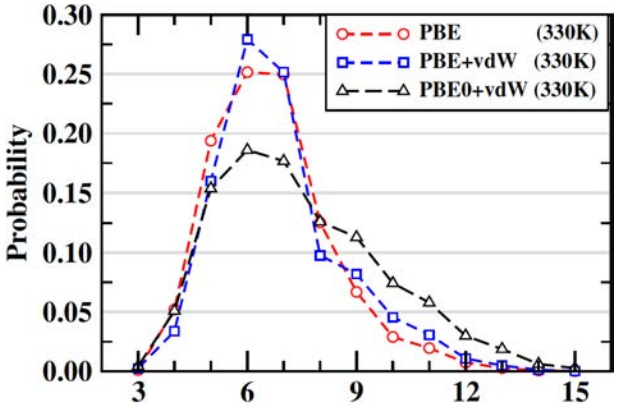
ACCURACY (DFT&NQE)

Classical NpT simulations of neat water



	Water Density (g/cm^3)
PBE	0.868
PBE + vdW	1.007
PBE0 + vdW	1.014

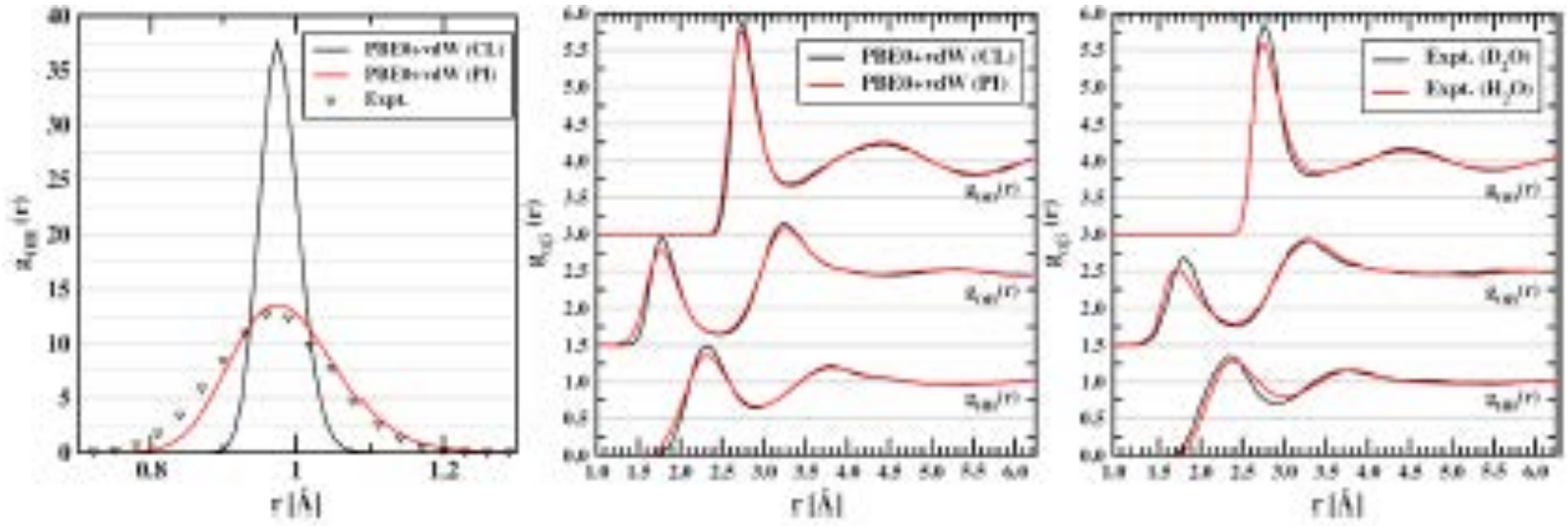
vdW = self-consistent TS scheme



Only vdW inclusive hybrid functional gives a water that is fluid at temperature not too far from room T

NQE from NVT PI-AIMD simulations using colored noise technique of Ceriotti&Parrinello (8 beads)

Preliminary Results



These simulations adopted strict adiabaticity (BO) criteria, accurate pseudopotentials and converged PW expansions.

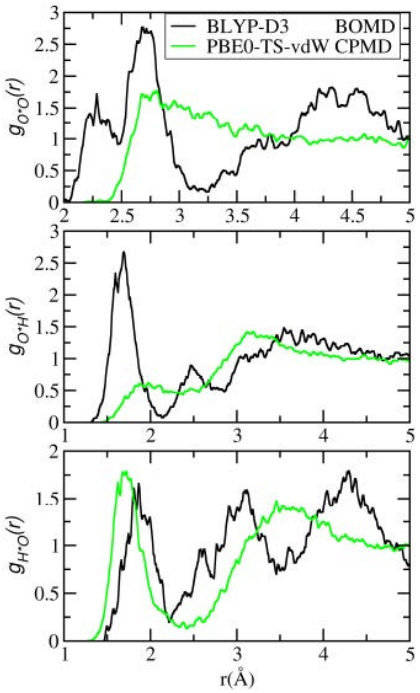
Need for vdW inclusive hybrid functional – still some slight overstructuring remains (residual functional deficiency?)

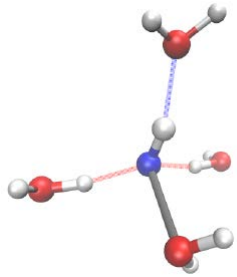
Water ions: PBE0+vdW enhances the difference between hydroxyl and hydronium – this has important consequences on proton transfer

OH^-	Average Accepting	Average Donating
PBE	3.54	0.66
PBE+vdW	3.66	0.78
PBE0+vdW	3.89	0.49

H_3O^+	Average Accepting	Average Donating
PBE	-	2.99
PBE+vdW	-	2.99
PBE0+vdW	-	2.99

Hybrid+vdW has a very dramatic effect on the structure of the solvated hydroxyl radical





Hemibond structure (see above) from self-interaction error results in a very stable and wrong complex: this deficiency is completely eliminated by vdW inclusive hybrid!

PBE0+vdW structures also improve XAS spectra and the position of the levels of a solvated Cl^- ion

…See Poster from Temple Team for further details

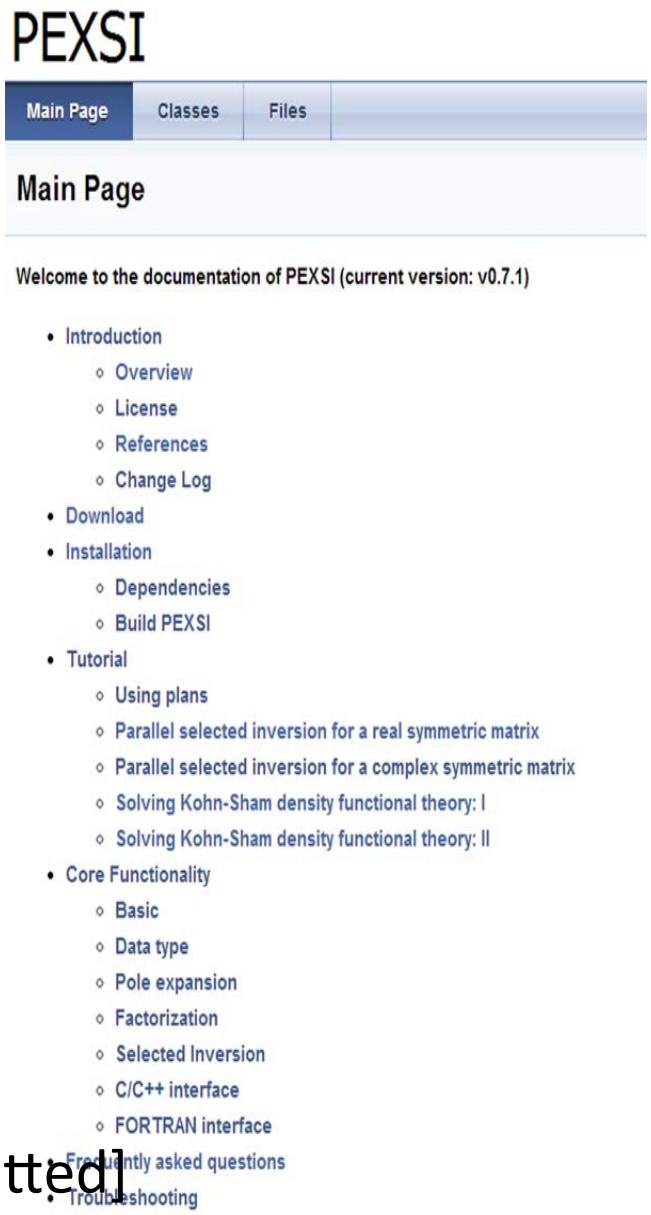
The large scale challenge

Collaboration with FASTMATH on Pole Expansion and Selected Inversion Method for Accelerating Electronic Structure Calculations

PEXSI

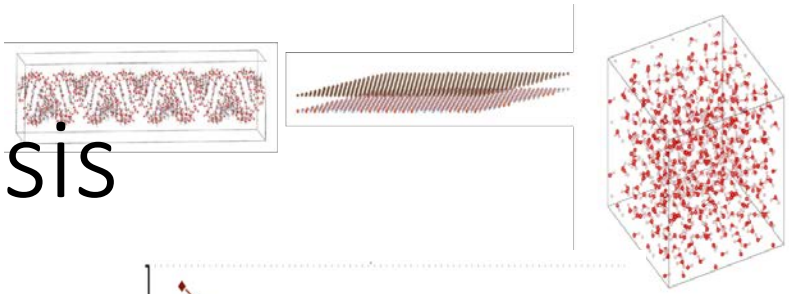
The PEXSI library is available online http://pexsi.org/, BSD license

- Integrated with SIESTA for accelerating atomic-orbital based calculation
- Being integrated into CP2K and other electronic structure packages.
- Massively parallel to 10,000 – 100,000 processors on high performance computers

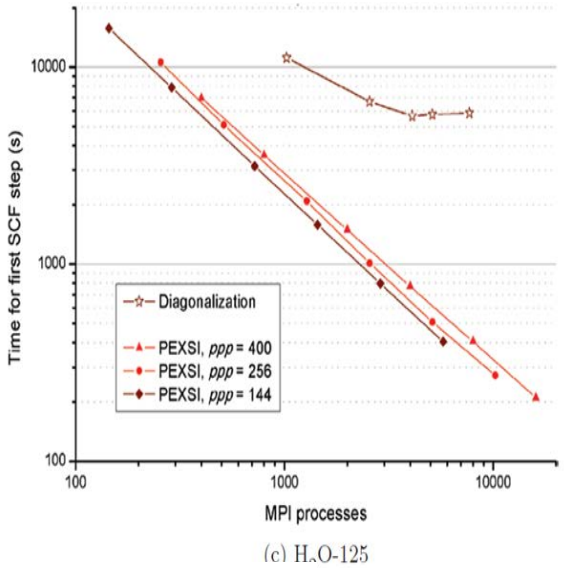


[M. Jacquelin, L. Lin and C. Yang, submitted]

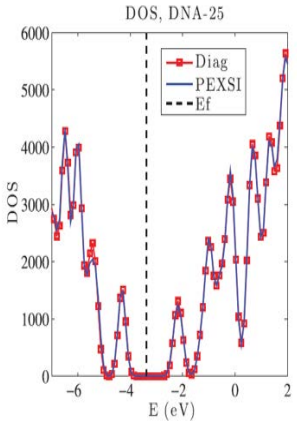
PEXSI for SIESTA basis

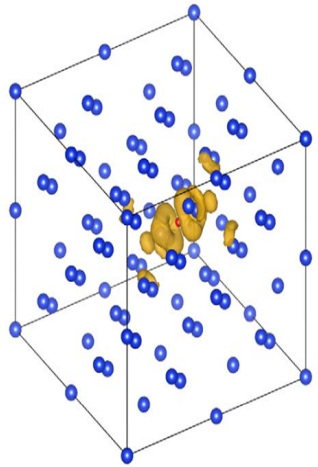


- SIESTA-PEXSI for DNA (quasi-1D, 17k atoms), C-BN (quasi-2D, 12k atoms), Water (3D, 24k atoms).
- Over 30 fold speedup for 3D water system with 24000 atoms
- Besides energies and forces, accurate calculation of other quantities such as DOS and LDOS



(c) H2O-125





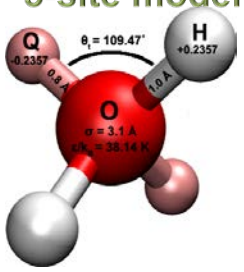
[L. Lin, A. Garcia, G. Huhs and C. Yang, JPCM 2014]

The time challenge:

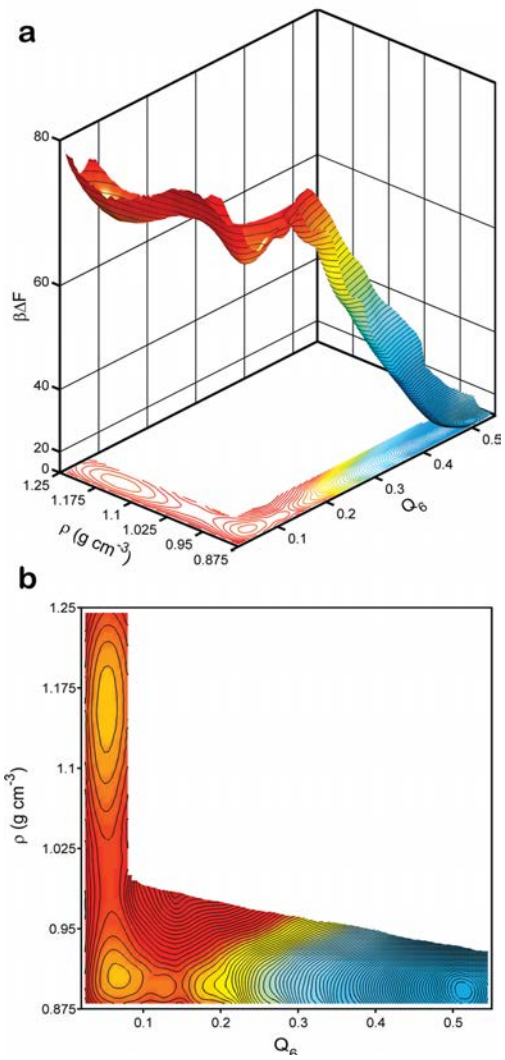
Sampling and Statistical Mechanics

Liquid-Liquid coexistence at deeply undercooled conditions?

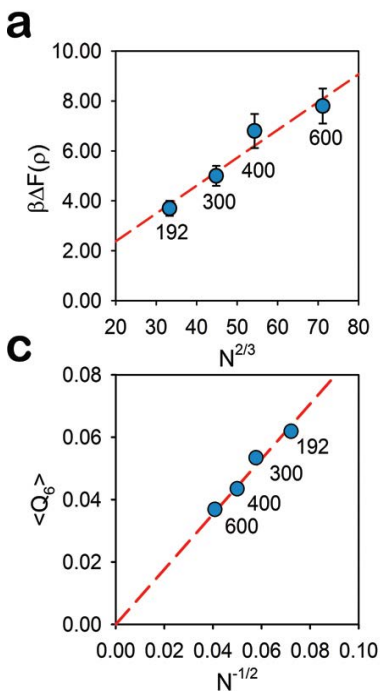
ST2 Water,
5-site model

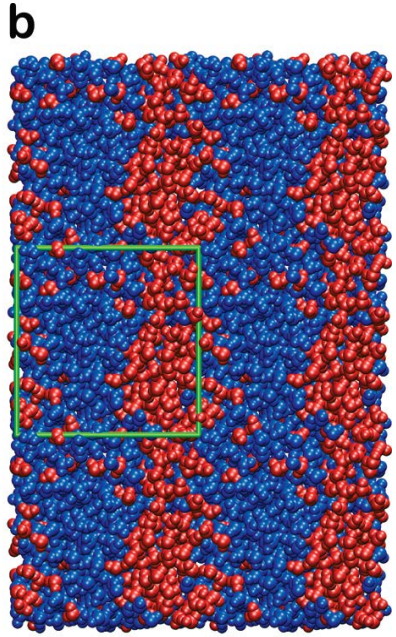


Model potential needed to sample times of order microsec



Finite size scaling





(J.C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, P.G. Debenedetti, *Nature,* June 19, 2014)

More efficient sampling methodologies are under development in the Princeton Applied Math Team (Weinan E and Amit Samanta)

Free energy surface reconstruction (Inverse problem)

Motivation: Obtain free energy surfaces from the knowledge of mean forces ($\mathbf{f}$) on the collective variables

- Expand free energy in terms of radial basis functions (RBF) at centers $z_1, z_2, \ldots, z_K$:

$$\mathcal{A}(\mathbf{z}) = \sum_{j=1}^{K} a_j \phi_\sigma \left(|\mathbf{z} - \mathbf{z}_j|^2 \right), \qquad \phi_\sigma(r) = e^{-r/2\sigma^2}$$

  The $z_1, z_2, \ldots, z_K$ are selected using k-means or spectral clustering

- Obtain optimal coefficients with proper regularization

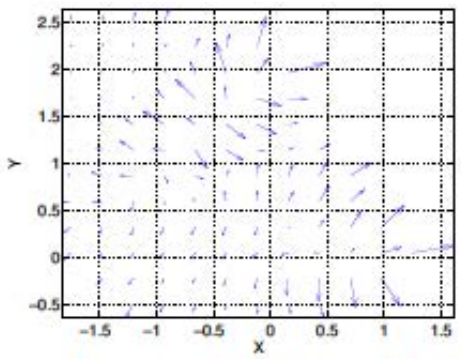
$$\mathbf{a} = \operatorname{argmin} \mathcal{E}(\sigma, \lambda, \mathcal{A}, \mathbf{f})$$

$$\mathcal{E}(\sigma, \lambda, \mathcal{A}, \mathbf{f}) = \frac{1}{K} \sum_{j=1}^{K} \left(|\nabla_z \mathcal{A}(\mathbf{z}_j) + \mathbf{f}_j)|^2 + \lambda |a_j|^2 \right)$$

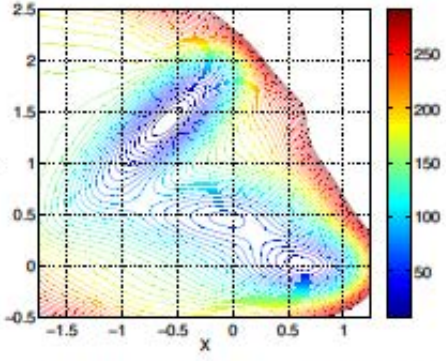
  The mean forces are stochastic quantities and regularization helps in minimizing the effect of noise in the data

- Model validation using multi-fold cross-validation

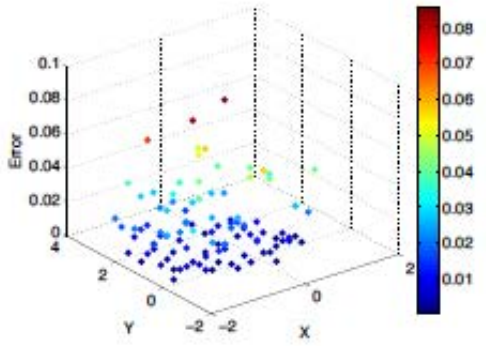
Examples: Muller potential, Melting of Copper



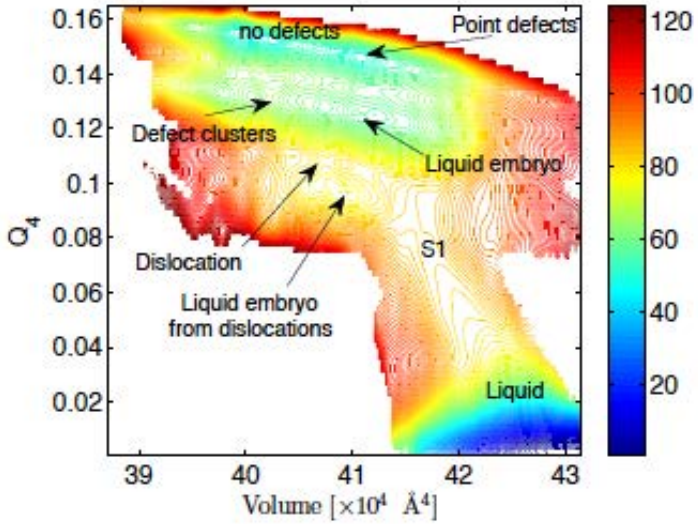
force distribution



reconstructed surface



relative error



- Gibb's free energy surface at 1350 K, 1 atm
- Multi-scale character, multiple metastable states
- Melting involves multiple barrier crossing events
- Elastic interaction play important role

Concluding remarks

- **Science**
- **Code implementation**
- **Applications**