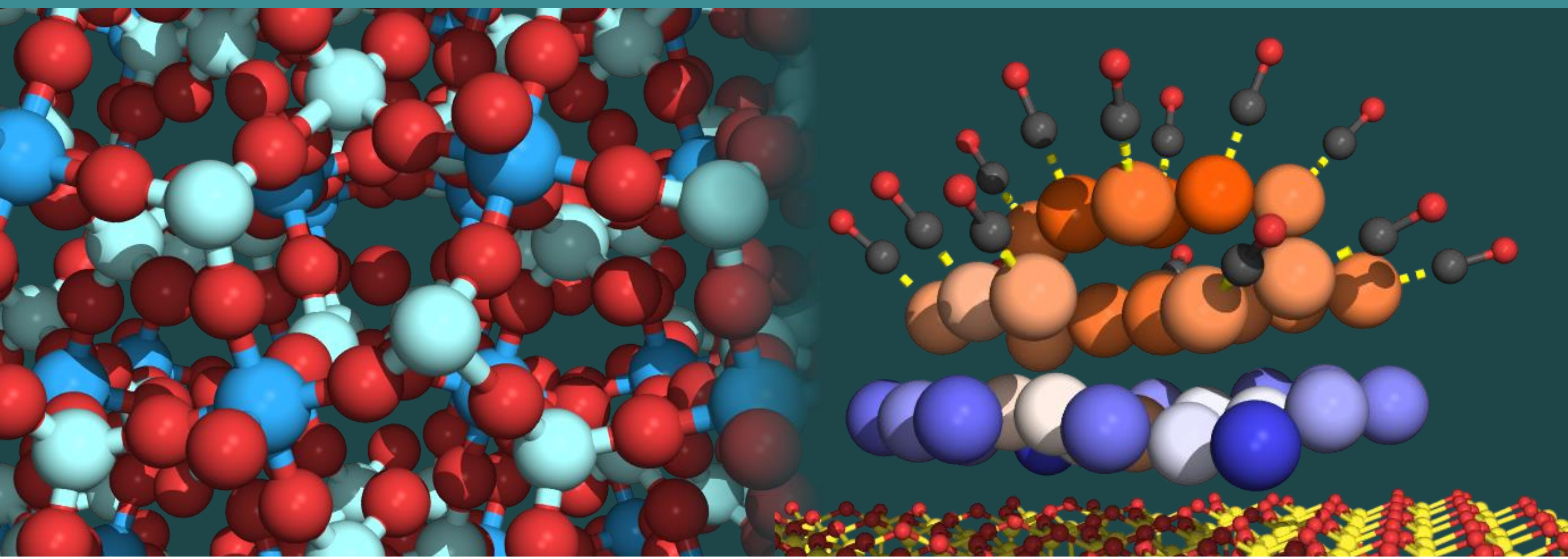
Parallel calculations of vibrational properties in complex materials: negative thermal expansion and elastic inhomogeneity

F.D. Vila and J. J. Rehr



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Vibrational Properties and Disorder

Vibrational Properties key to:

- Materials:
  - Finite temperature effects → Phase diagrams
  - Unusual properties (Negative Thermal Expansion)
  - Catalysis: Reactivity
- Spectroscopy:
  - Damping and broadening (EXAFS and XRD MSRD)

Inhomogeneity:

- Structural disorder effects on vibrations in complex systems?

Problem:

- Very large/complex systems → Computationally intractable

Previous Work

PRB

Theoretical x-ray absorption Debye-Waller factors

Fernando D. Vila, J. J. Rehr, H. H. Rossner, and H. J. Krappe

Phys. Rev. B **76**, 014301 (2007) - Published 5 July 2007

PRB Editors' Suggestion

X-ray absorption Debye-Waller factors from *ab initio* molecular dynamics

F. D. Vila, V. E. Lindahl, and J. J. Rehr

Phys. Rev. B **85**, 024303 (2012) - Published 25 January 2012

Ab initio Vibrational Properties Summary

Projected Vibrational DOS: Use efficient pole model

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\,\mathrm{Im}\left\langle 0 \left| \frac{1}{\omega^2 - \mathbf{D} + i\varepsilon} \right| 0 \right\rangle \cong \sum_{v=1}^{N} w_v \delta(\omega - \omega_v)$$

EXAFS MSRDs:

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\int_0^\infty \frac{1}{\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right)\rho_R(\omega)\,d\omega$$

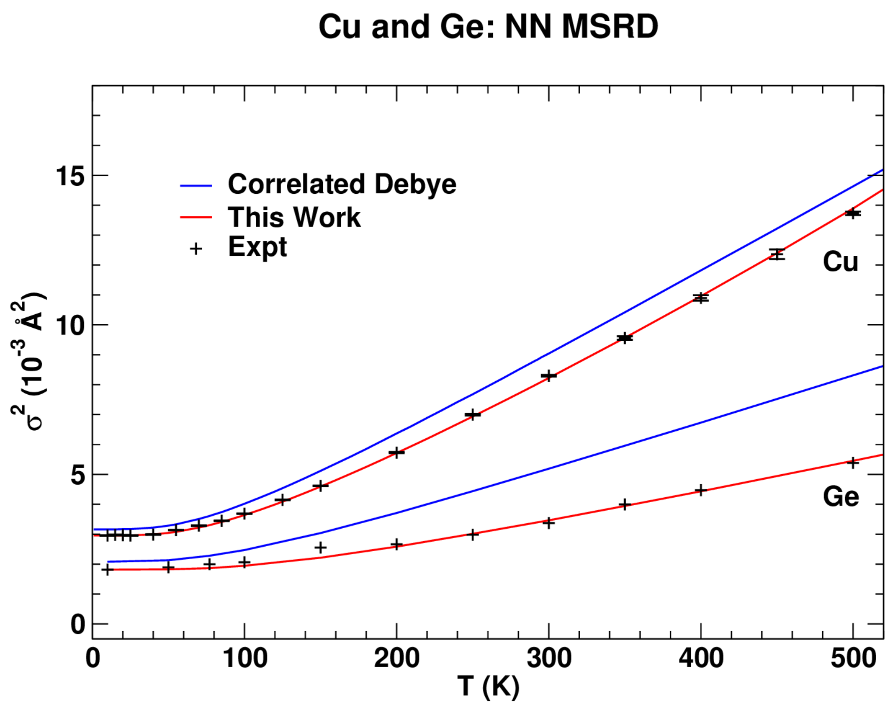
Helmholtz Free Energy:

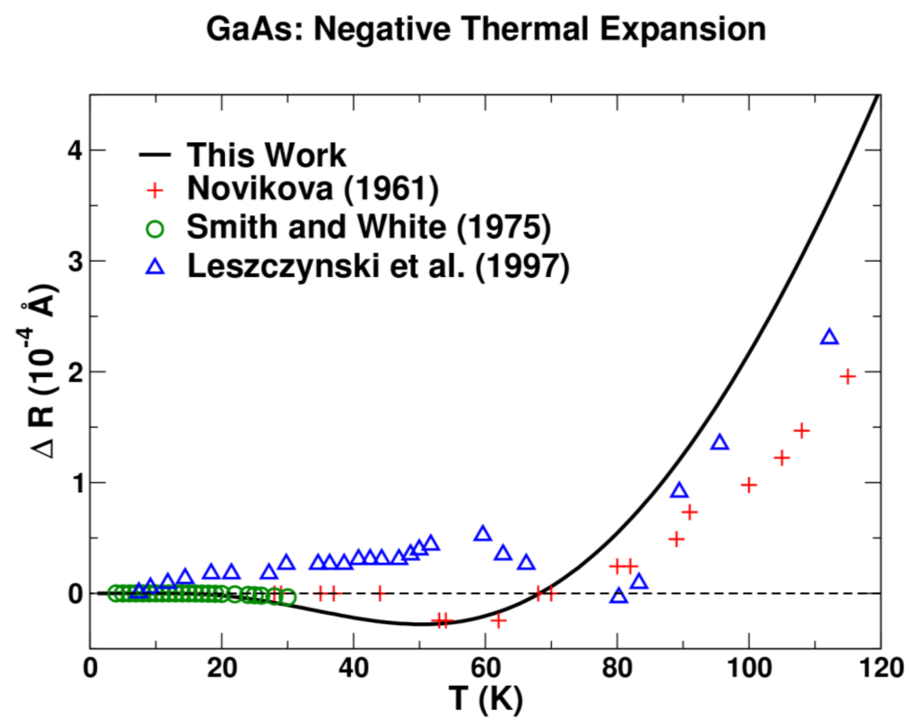
$$F(T) = E + k_B T \sum_i^{N_{coor}} \int_0^\infty \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\rho_i(\omega)\,d\omega$$

Mean Einstein temperatures:

$$T_E = \frac{\hbar\langle\omega^2\rangle^{-\frac{1}{2}}}{k_B} = \frac{\hbar}{k_B}\left(\sum_{v=1}^{N}\frac{w_v}{\omega_v^2}\right)^{-\frac{1}{2}}$$

Typical Results





Key property: Dynamical Matrix D

In Reciprocal Space:

$$\widetilde{D}_{j\alpha,j'\beta}(\mathbf{q}) = \sum_{l'} D_{jl\alpha,j'l'\beta} \exp(i\mathbf{q}\cdot[\mathbf{r}(j'l') - \mathbf{r}(j0)])$$

FT

In Real Space:

$$D_{jl\alpha,j'l'\beta} = \left(M_j M_{j'}\right)^{-1/2} \frac{\partial^2 E}{\partial u_{jl\alpha} \partial u_{j'l'\beta}}$$

Finite Differences

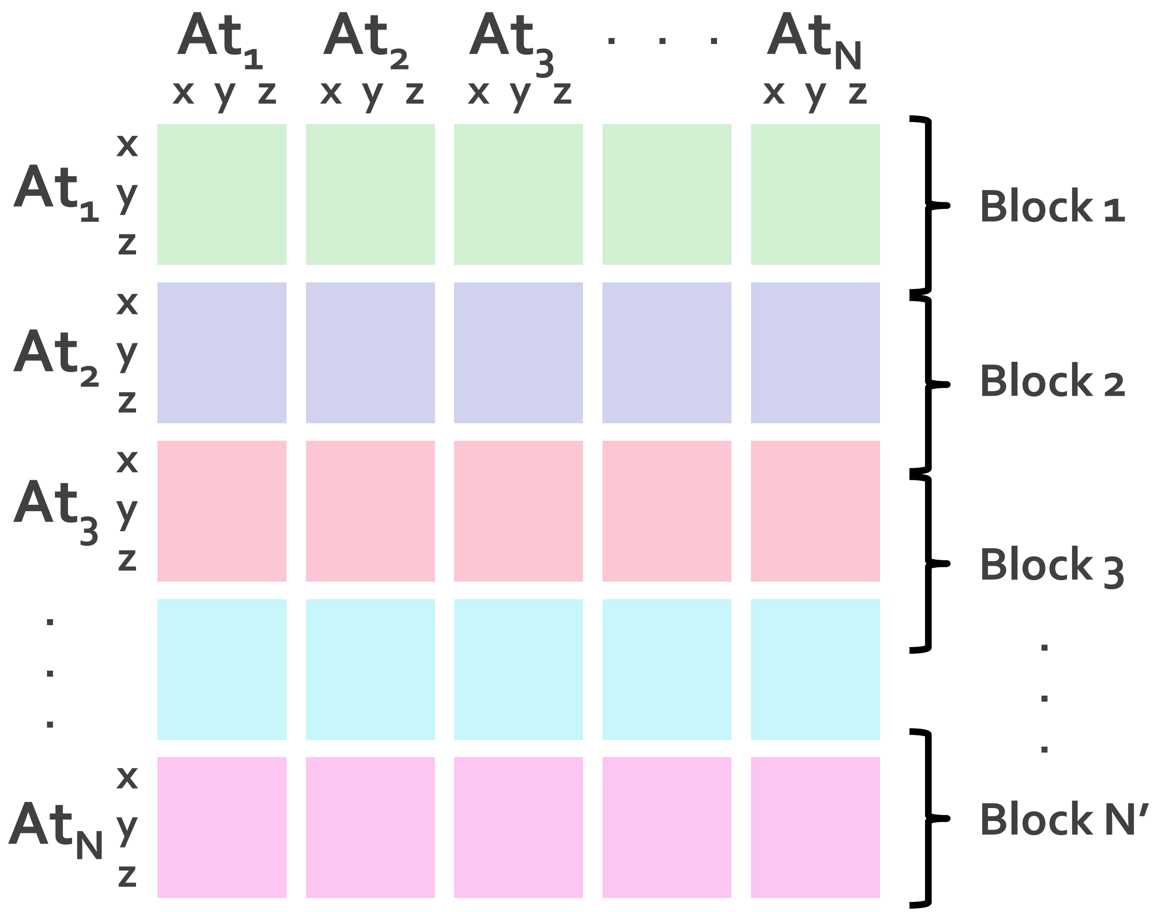
Real Space Forces:

$$D_{jl\alpha,j'l'\beta} = \left(M_j M_{j'}\right)^{-1/2} \frac{\partial F_{jl\alpha}}{\partial u_{j'l'\beta}}$$

Parallelizing the DM Calculation

Pt_{37} on SiO_2:
- 8 simult. blks
- ~69 coords/blk
- 72 cores/blk
- 4.5 wallclock hrs/blk

Pt_{37} on Graphite:
- 18 simult. blks
- ~54 coords/blk
- 72 cores/blk
- 4 wallclock hrs/blk



Example: EXAFS MSRDs in ZrW_2O_8

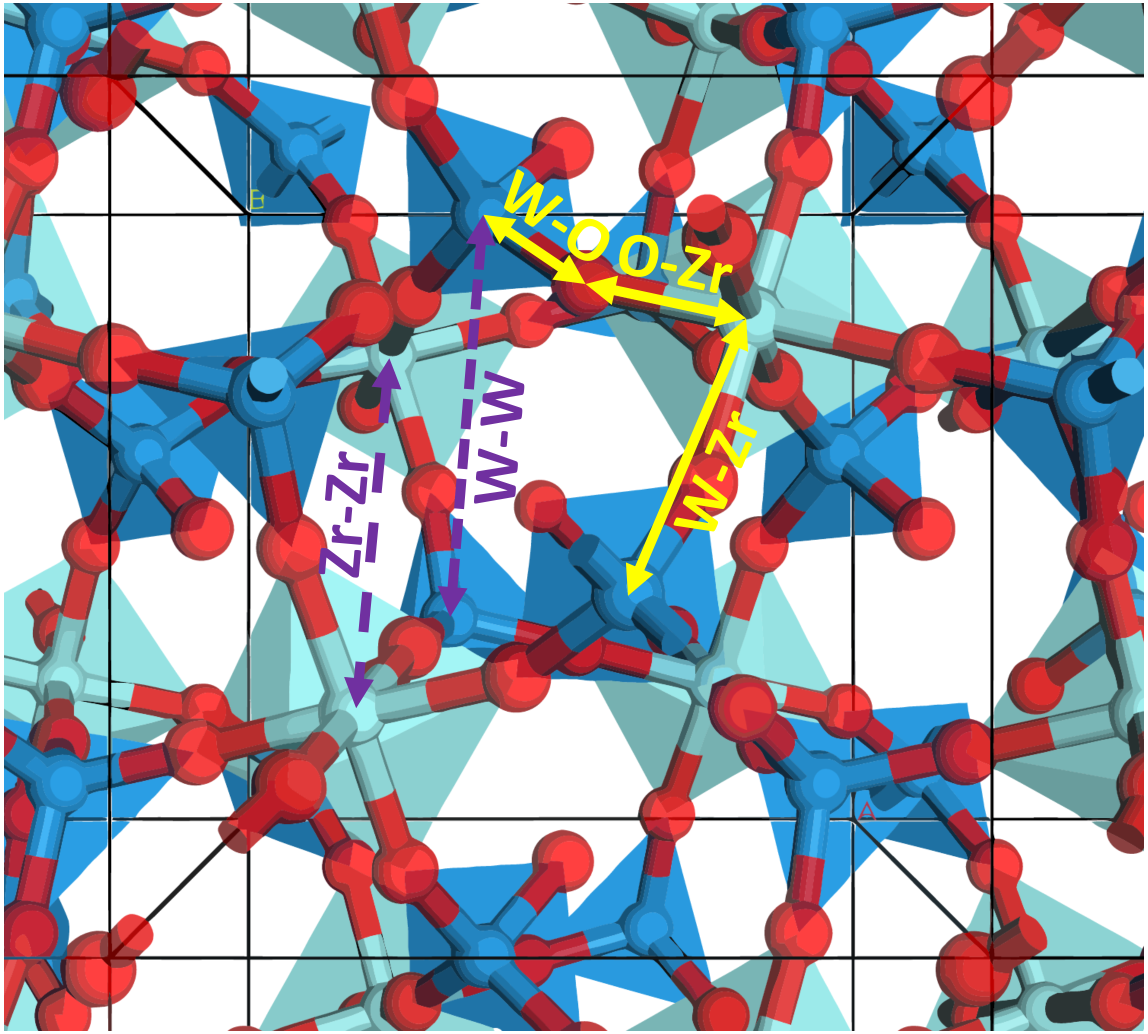
Very interesting system:

- Archetypical example of NTE from 10-1000 K
- Complex structure
- Difficult simulation with original DM approach

Methods summary:

- PBEsol/PAW optimization with 400 eV planewave cutoff
- Unit cell (44 atoms) to speed-up simulations

ZrW_2O_8: Complex unit cell



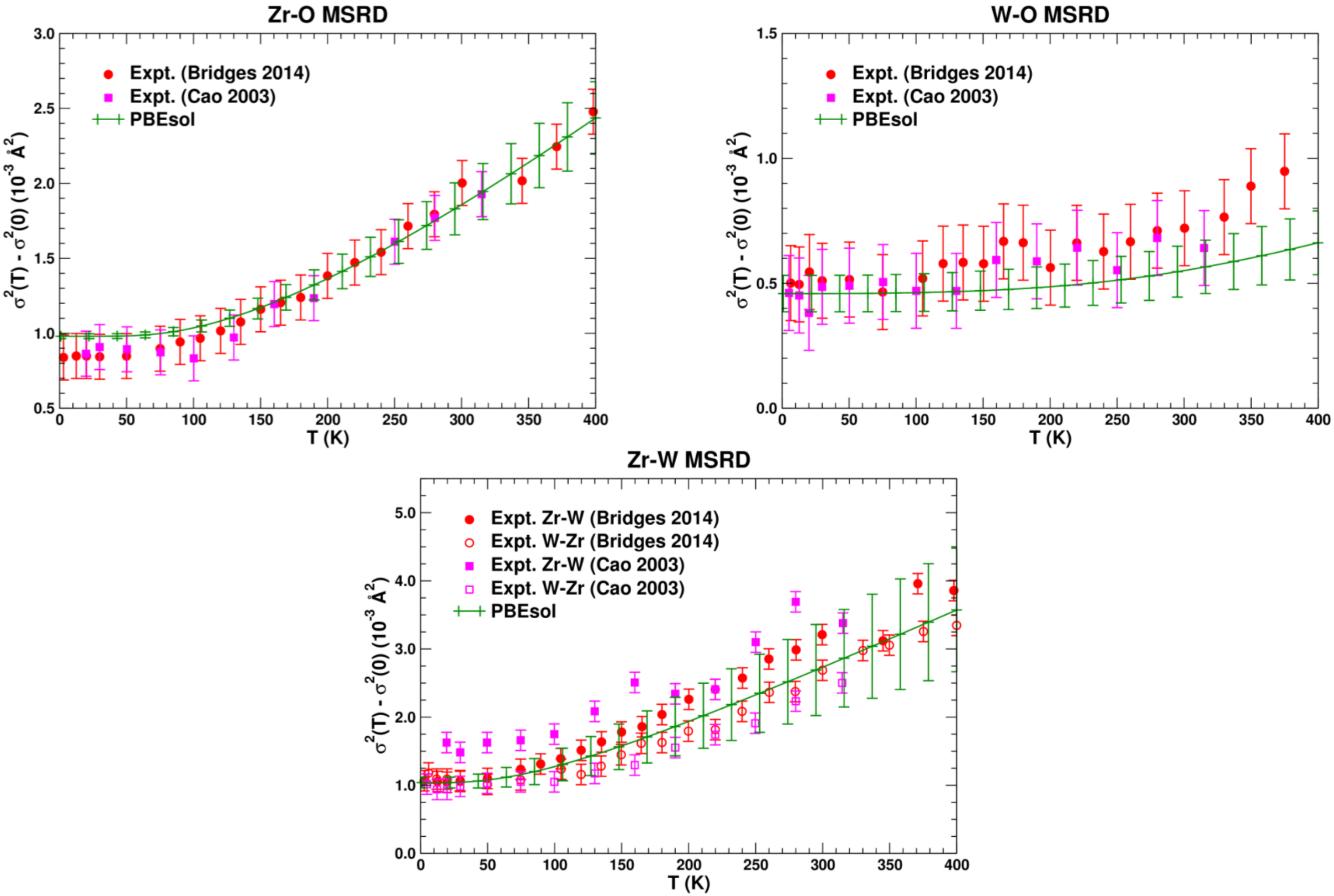
Accessible:

W-O: 1.796 Å
O-Zr: 2.090 Å
W-Zr: 3.855 Å

Need larger cell:

W-W: 4.674 Å
Zr-Zr: 6.567 Å

ZrW_2O_8: Mean-Squared Relative Displacements



Example: Elastic inhomogeneity in Pt_{37} on SiO_2

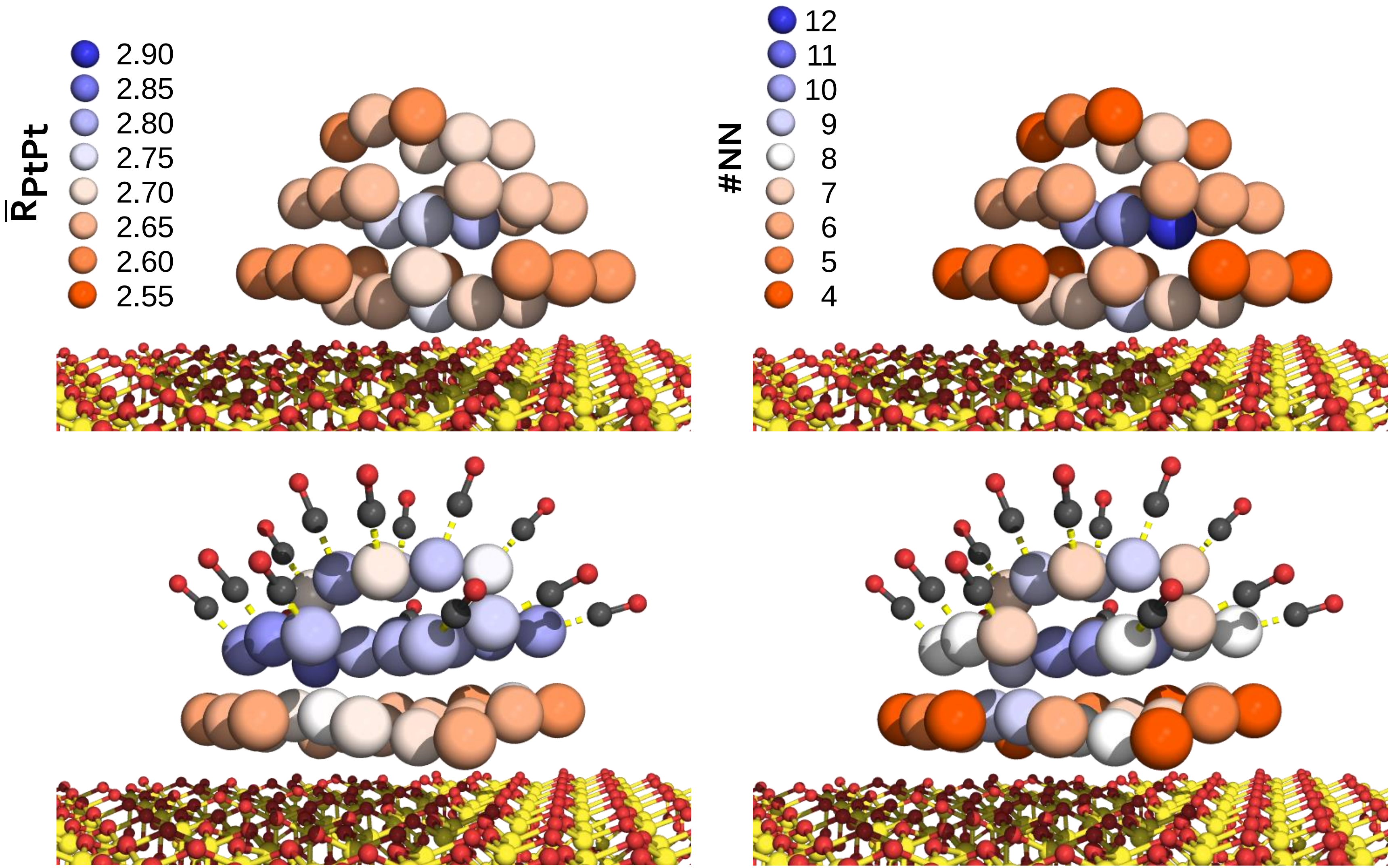
Critical for understanding catalysis:

- Expt. can only access average properties
- Surface-interior differences key to activity?
- Impossible with original DM approach

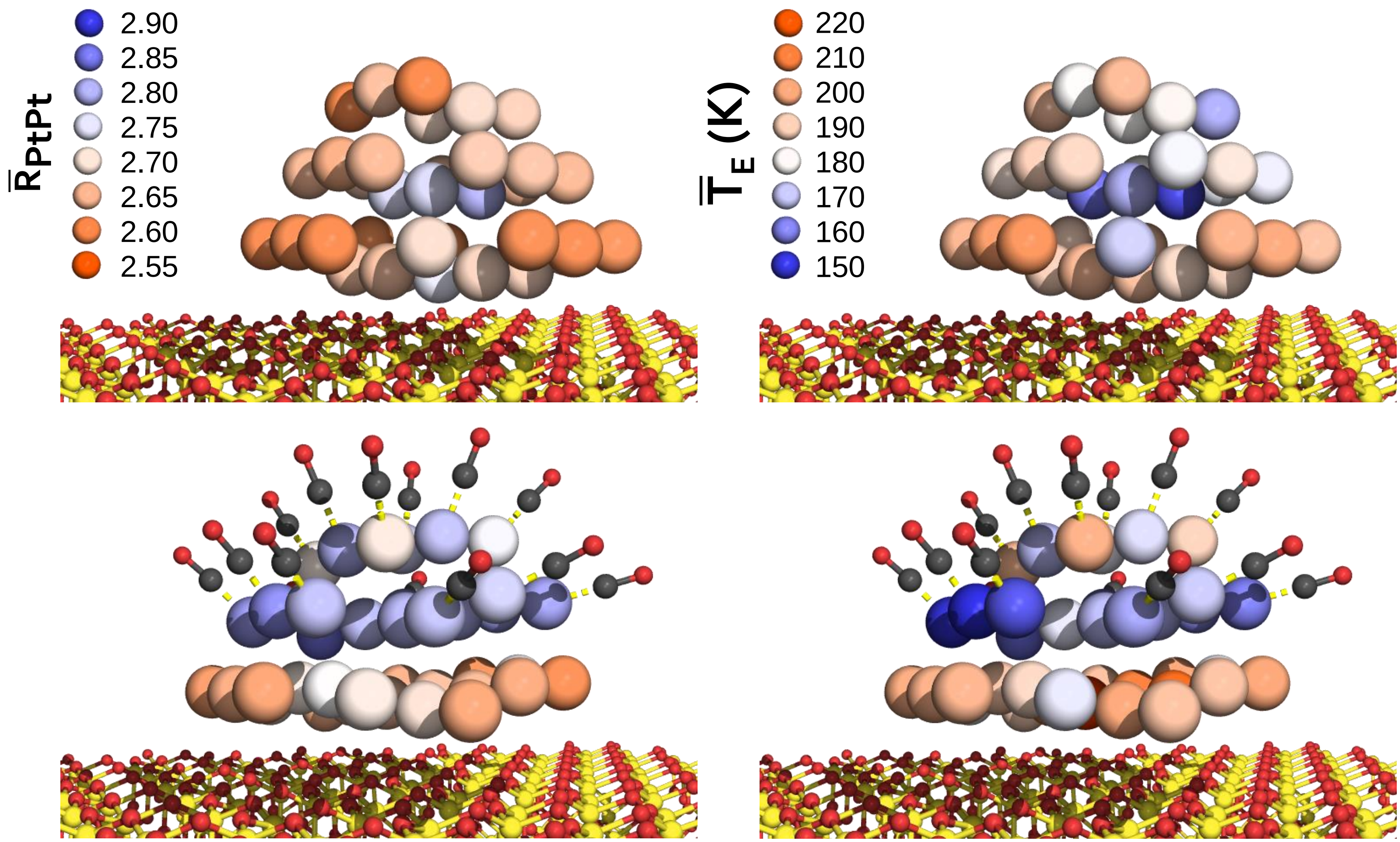
Methods summary:

- PBE/PAW optimization with 400 eV planewave cutoff
- SiO_2: reconstructed (001) α-quartz (2 x 4, 278 atoms)

Mean PtPt Bond Lengths *vs* # of Pt NN



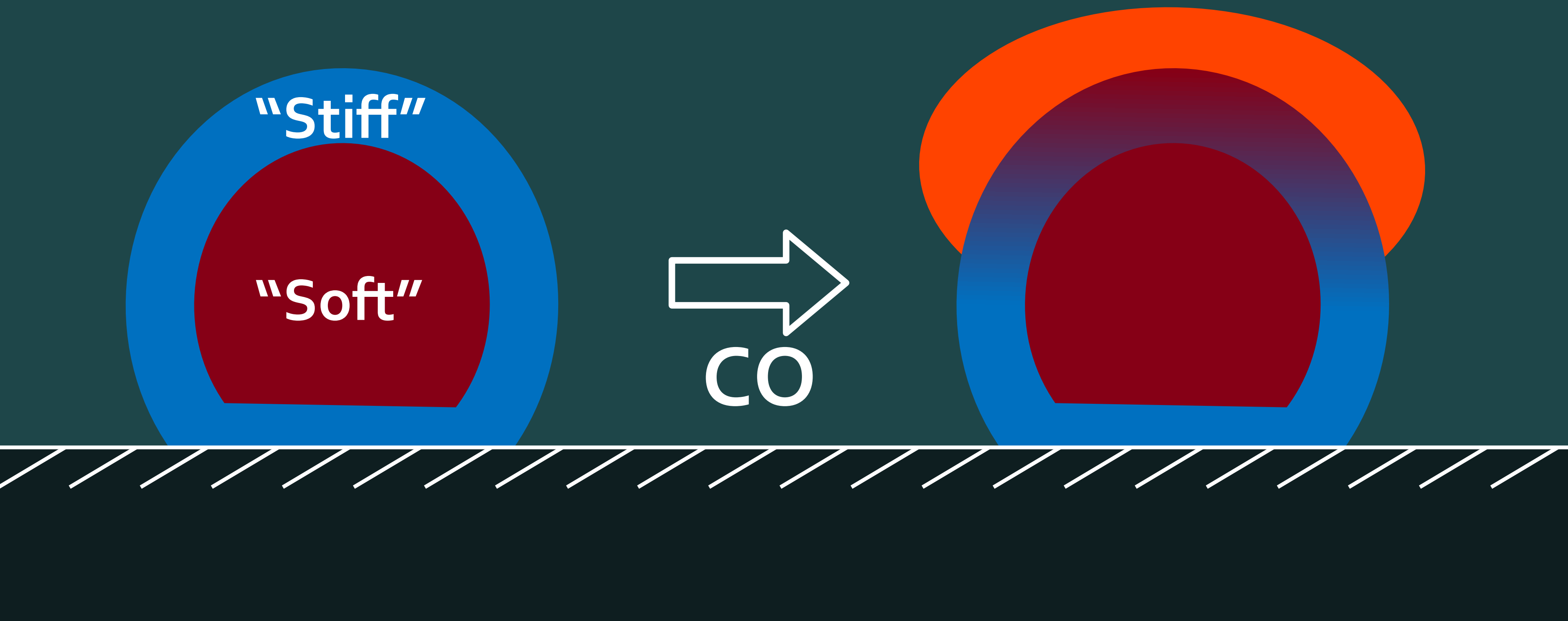
Mean PtPt Bond Lengths *vs* their Einstein Temp.



Model of Stiffness

Pt nanoparticles have:

- Stiff outer shell (Shorter R_{PtPt}, less #NN)
- Soft core (Longer R_{PtPt}, more #NN)
- Outer shell weakens upon CO adsorption



Conclusions

- Efficient dynamical matrix in real space:
    - Big unit cells
    - Flexible load distribution
- New insights into complex materials
    - Accurate MSRDs in ZrW_2O_8
    - "Hard shell" in supported Pt nanoparticles
    - Correlations between XAFS parameters
        - $\#NN \Leftrightarrow R_{\mathrm{PtPt}} \Leftrightarrow \nu_E \Leftrightarrow \sigma^2_{PtPt}$
- Future work
    - Deployment to Corvus workflow manager
    - Local approach for further efficiency

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