MMSNF 2013, Chicago, IL, Oct. 14-16, 2013

Thermodynamic Models of UO_2 and UN

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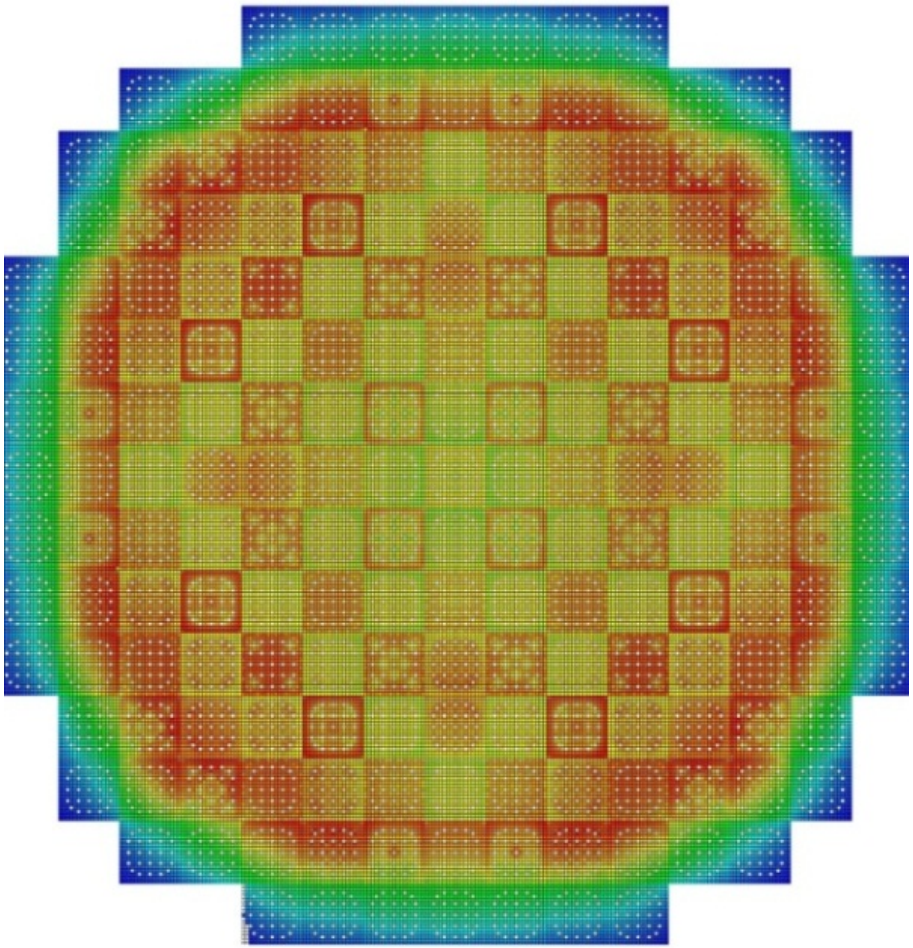
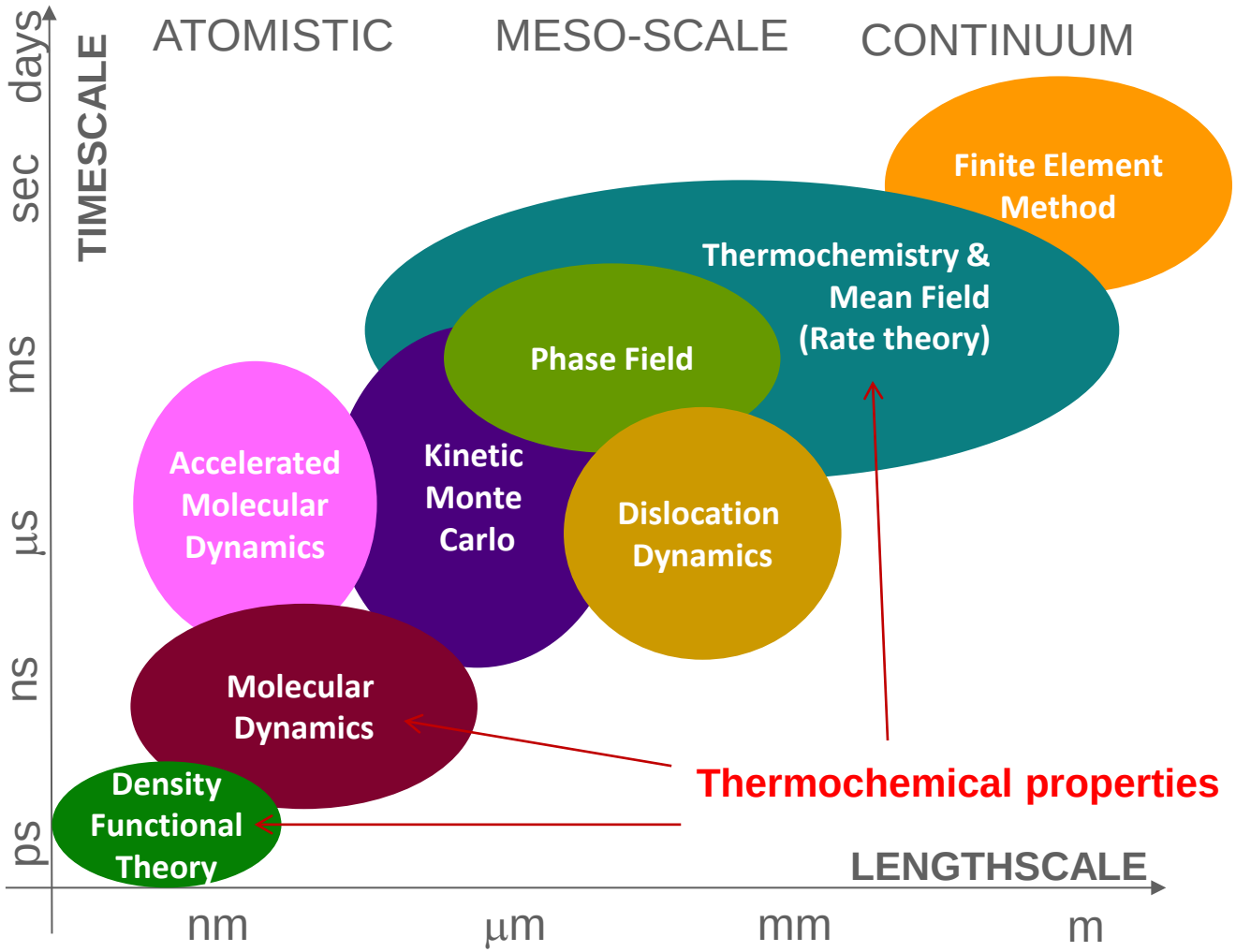
Controlled thermochemistry of nuclear fuels

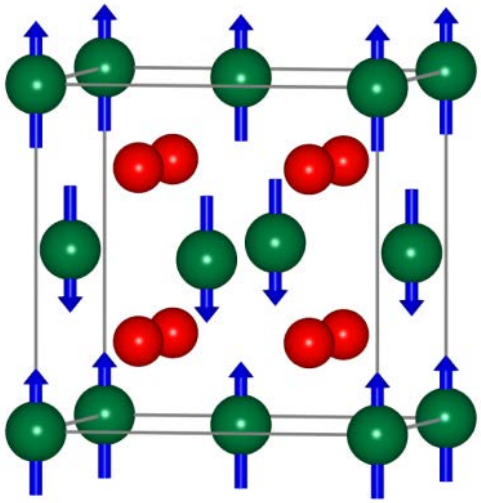


Multi-scale theoretical and computational methods



M. Stan, Materials Today, 12 (2009) 20.
R. Devanathan, *et al.*, Energy Env. Sc., 3 (2010) 1406

Uranium Dioxide



UO_2 has a fluorite structure

- green = U
- red = O
- arrows = magnetic ordering of U atoms
- Antiferomagnetic below T_N=30K.

P. Cristea et al. J. Optoelectr. Adv. Mat, 9 (2007) 1750.

Potentials

- Morelon [1] and Basak [2] potentials find accurate defect energetics but are not fit for phonons

- Read [3] potential finds accurate phonon dispersions but is not fit for defect energetics

[1] Morelon et al., Phil. Mag. 83 (2003)
[2] Basak et al., J. Alloys Comp. 360 (2003)
[3] M.S.D. Read and R.A. Jackson, J. Nucl. Mater. 406 (2010) 293

The Iterative Potential Refinement (IPR)

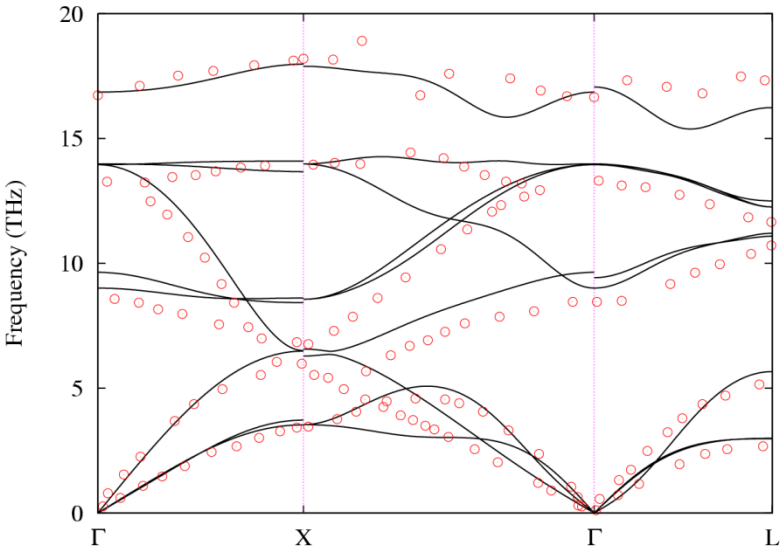
Comparison of Potential Forms			
	Basak	Morelon	Read
O-O	Buckingham	Four-range Buckingham	Four-range Buckingham
O-U	Buckingham, Morse	Buckingham	Buckingham
U-U	Buckingham	-	-
Charges	Formal	Non-formal	Formal
Shells	no	no	yes

IPR can predict forces, stresses, and **energies**

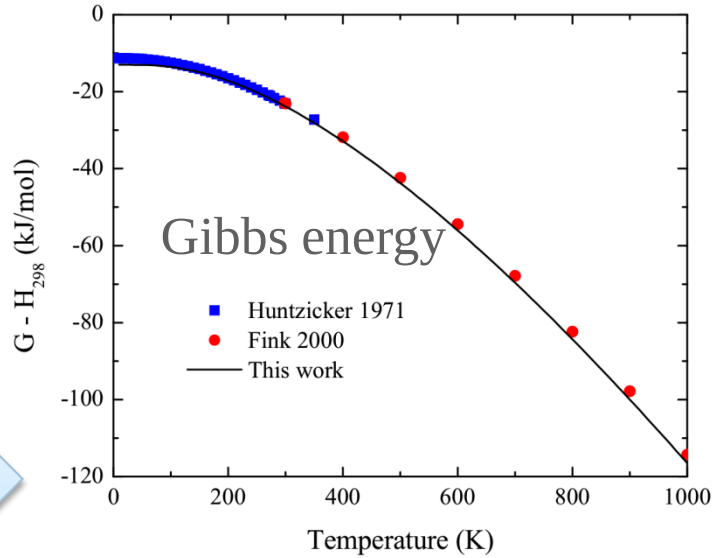
A. Thompson et al., Phys Rev. B (2013) in press

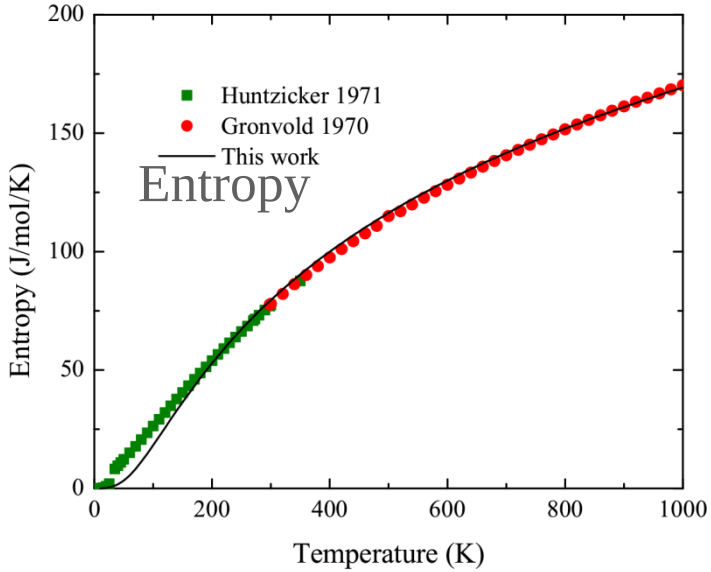
Thermodynamic properties of UO_2 by Density Functional Theory (DFT)

$$G = H - TS$$



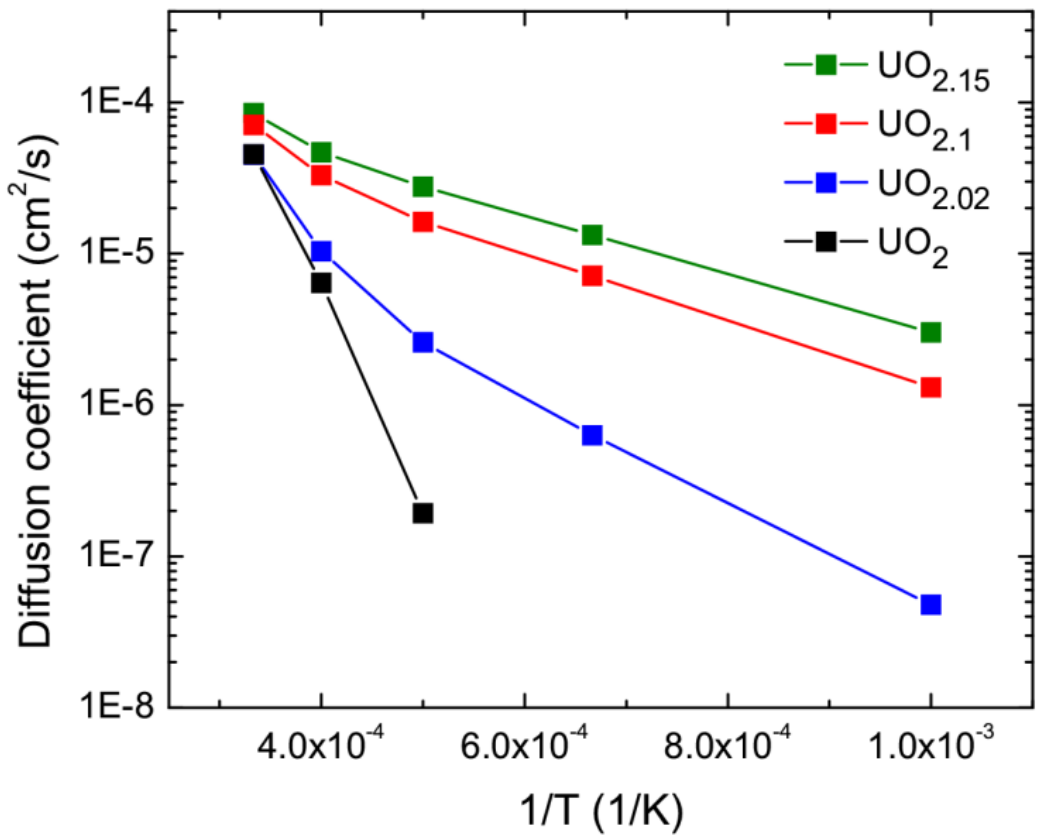
Calculated phonon spectrum of UO_2 compared with measurement using inelastic neutron scattering by Dolling [1]





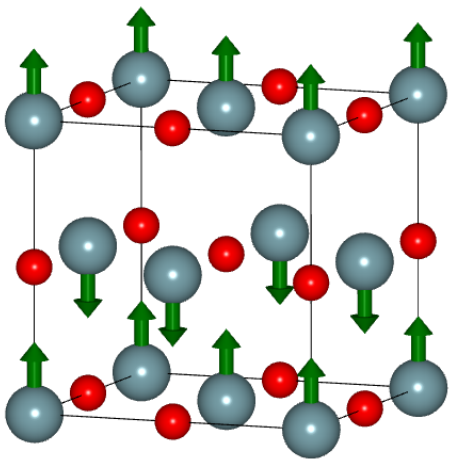
[1] Dolling et al., Canadian Journal of Physics 43 (1965)

Oxygen diffusion in UO_{2+x} by Molecular Dynamics (MD)



Z. G. Mei et al. (2013) in preparation

Uranium Nitride

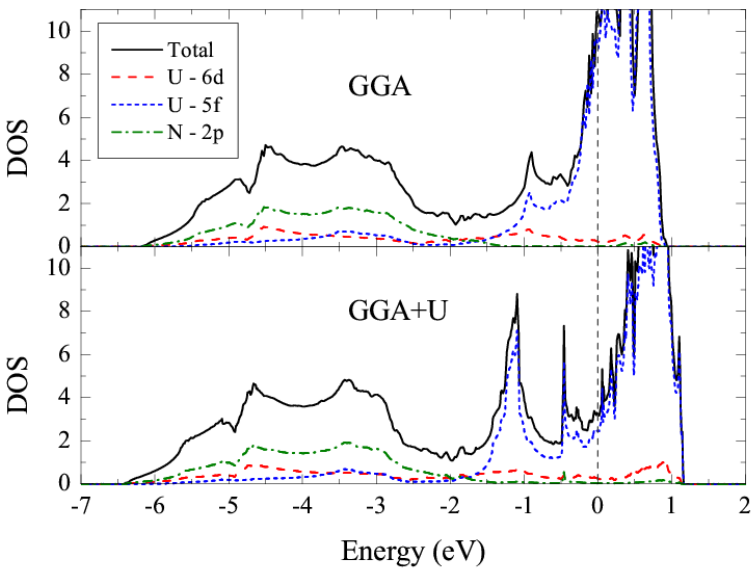


Potential nuclear fuel for future generation nuclear reactors

- High melting point
- High thermal conductivity
- High uranium density
- Good compatibility with Na coolant

Crystal structure of uranium nitride (UN):

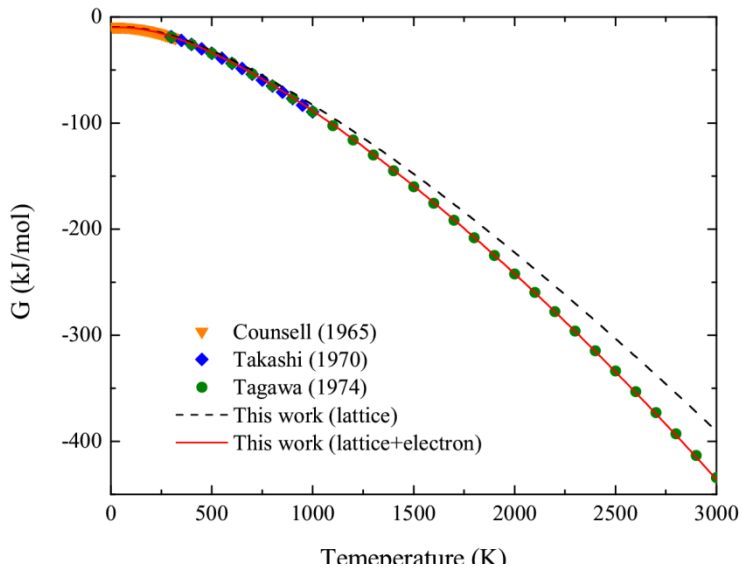
- Antiferromagnetic (AFM) structure below T_N=53K

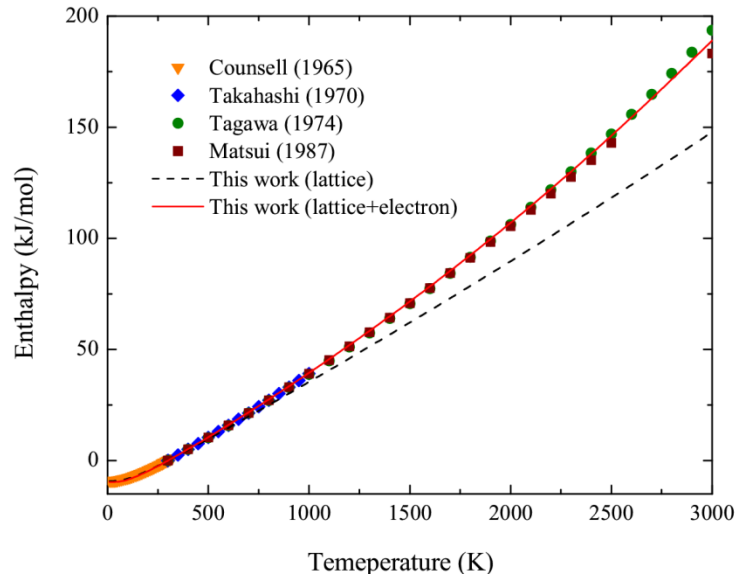


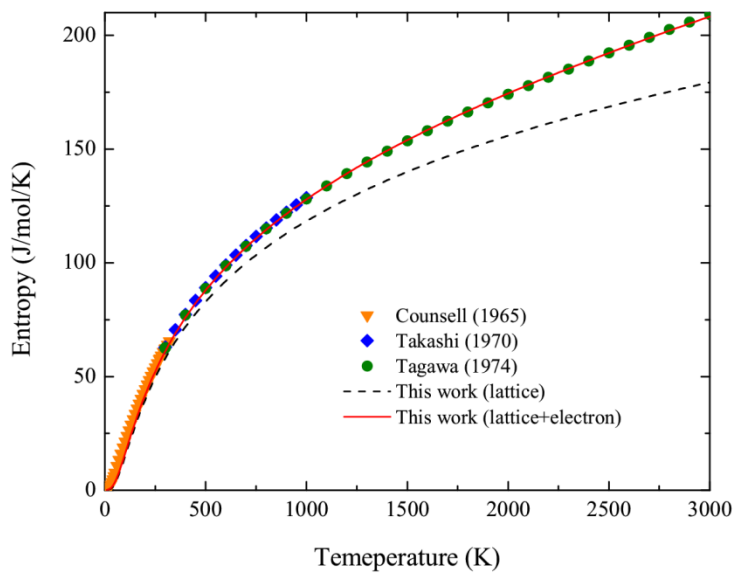
- UN shows a metallic character
- The calculated electron density of state (DOS) by DFT using both GGA and GGA+U methods show no band gap (metal).

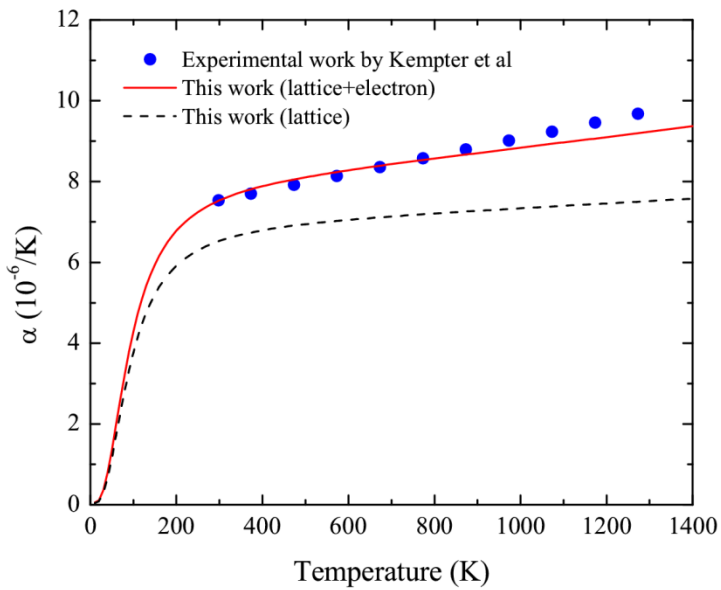
Thermodynamic Properties of UN by DFT

See PA12









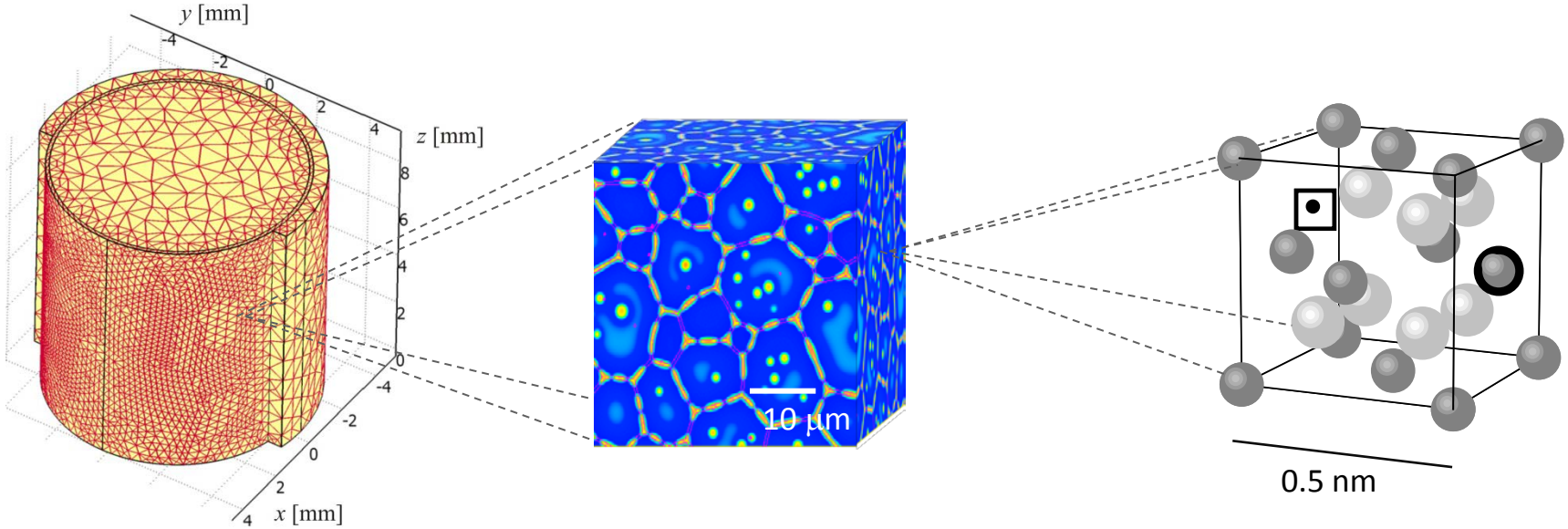
Z. G. Mei et al, J. Nucl. Mater, 440 (2013) 63

Computational Microscopy: sampling and scale bridging

Transport and deformation
(Finite Element Method)

Microstructure evolution
(Phase Field Method)

Defect formation/phase nucleation
(Ab Initio Molecular Dynamics)



Bridging scales expands the investigation time and space domains.
- Lower scales help improve the understanding of underlying mechanisms.
- Higher scales help improve the prediction of global properties.

ZOOM - a multi-scale computational microscope (ANL-Univ. of Chicago)
Contact mstan@uchicago.edu

M. Stan, in Characterization of Materials, John Wiley & Sons, 2012.

Conclusions

- Thermodynamic properties of nuclear fuels (UO_{2+x}, UN) strongly depend on temperature and deviation from stoichiometry
- The IPR potential was optimized for accurate phonon and energy calculations of UO_{2+x} free energy and O diffusivity
- Phonon-electron coupling is critical for UN calculations of free energy and thermal expansion
- Sampling and scale bridging expand the investigation time and space allowing for computational microscopy.