The Thermal Neutron Scattering Law for Hydrogen Bound in Plutonium Dihydride and Predicted Critical Mass for Several Configurations

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Outline

- Background
  - Phase Diagram
  - Crystal Structure
- DFT/LD Calculations
- TSL Evaluation
- Calculated Critical Mass
  - Bare Sphere
  - Water-reflected Sphere
- Conclusions

Plutonium-Hydrogen Phase Diagram

- H$_2$ (gas) reacts with Pu (metal) to form plutonium hydrides (PuH$_x$)

- Three PuH$_x$ phases present
  - PuH$_2$ (FCC) for H/Pu ≤ 2.0
    - Two phase solid solution of Pu (metal) + PuH$_2$ (FCC)
  - PuH$_{2+x}$ (FCC) for 2.0 < H/Pu < 3
    - Single phase solid solution for 2.0 < H/Pu < 2.75
    - Two phase solid solution, PuH$_{2+x}$ (FCC) + PuH$_3$ (Hex) for 2.75 < H/Pu < 3-ε
  - PuH$_3$ (Hex) for 2.75 < H/Pu ≤ 3.0
    - Single phase solid solution for 3-ε < H/Pu < 3.0

- This work concentrates on PuH$_2$
  - PuH$_{2+x}$ and PuH$_3$ to be evaluated later
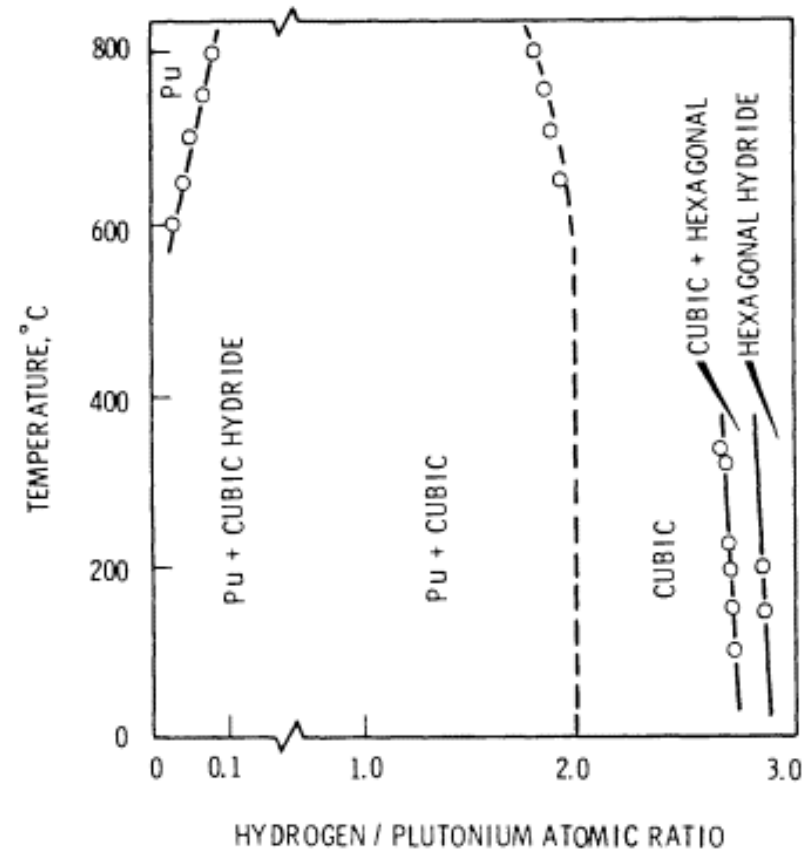
Phase diagram for the plutonium-hydrogen system. From R. N. R. Mulford and G. E. Sturdy, *J. Am. Chem. Soc.*, **78**, 3899 (1956).
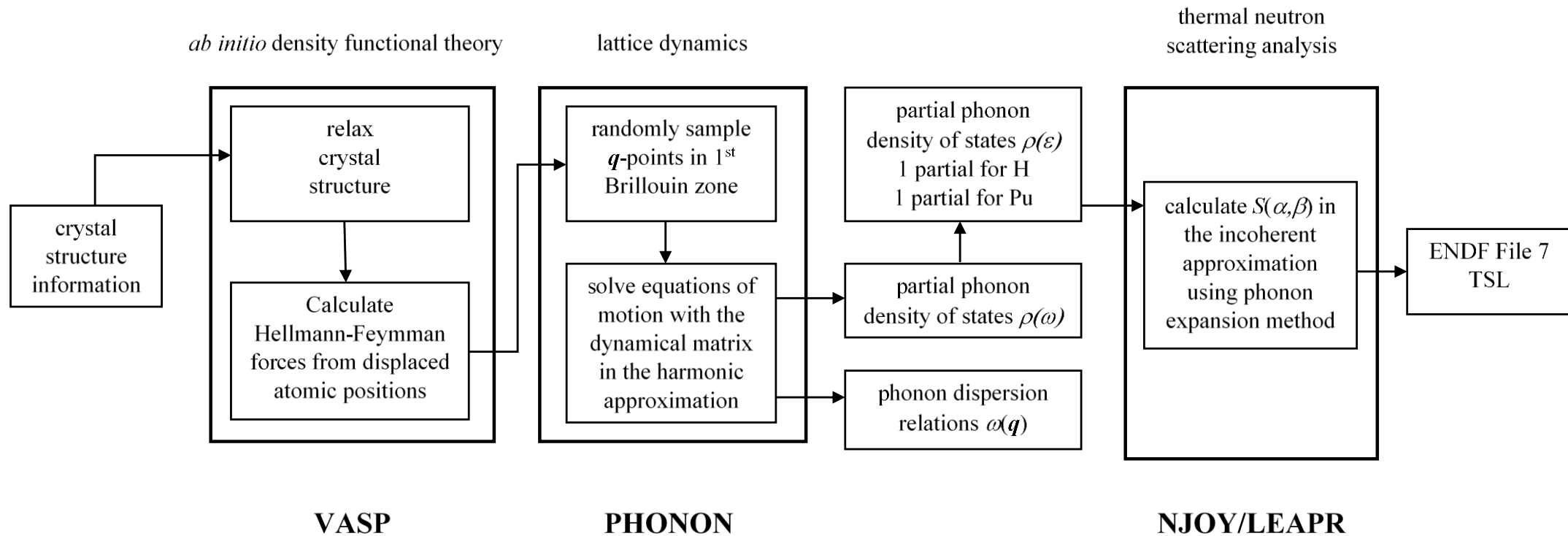
PuH$_2$ Structure

- PuH$_2$ has a CaF$_2$ type FCC structure
  - 12 atoms per unit cell
  - 4 Pu atoms (blue) at vertices and faces of unit cell
  - 8 H atoms (grey) in tetrahedral holes between Pu atoms
  - Mass density of 10.40 g/cm^3

- Measured lattice parameter (X-ray diffraction)
  - a = 5.359 ± 0.002 Å, Mulford and Sturdy (1955)
  - a = 5.359 ± 0.001 Å, Coffinberry and Ellinger (1956)
  - a = 5.359 ± 0.002 Å, Muromura et al. (1972)
  - a = 5.3593 Å, Willis et al. (1985)

- H-PuH$_2$ TSL developed using first-principles approach
  - Density Functional Theory (DFT) to calculate interatomic Hellman-Feynman forces for crystal structure
  - Lattice Dynamics (LD) to determine dispersion relations and phonon density of states (DOS)
 - H-PuH$_2$ TSL evaluated in incoherent approximation using NJOY/LEAPR
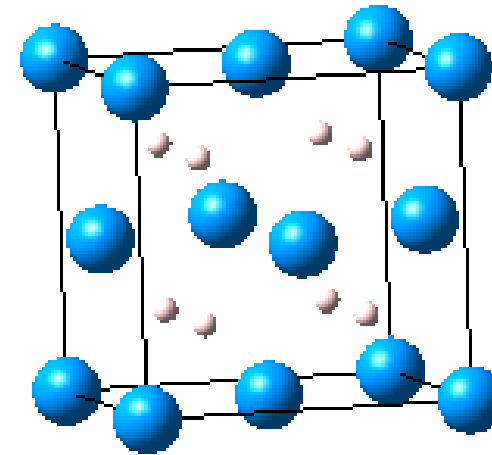
PuH$_2$ Unit Cell

TSL Evaluation Process using First-principles DFT/LD Calculations

# PuH$_2$ Structure Optimization

- DFT structure optimization using VASP (*Vienna Ab-Initio Simulation Package*)
  - GGA exchange and correlation functional
  - Hubbard *U* parameter correction applied to Pu 5*f* electrons
    - Account for effect of strong correlation of 5*f* electrons on chemical binding of U and Pu molecules
  - Spin-polarized magnetism
  - 500 eV planewave cutoff
  - *k*-point spacing of 0.2 Å^{-1} (11×11×11 k-mesh)
  - 10^{-6} eV total electronic energy threshold

- **Hubbard U = 0.6 eV reproduces the measured lattice parameter of *a* = 5.349 Å**
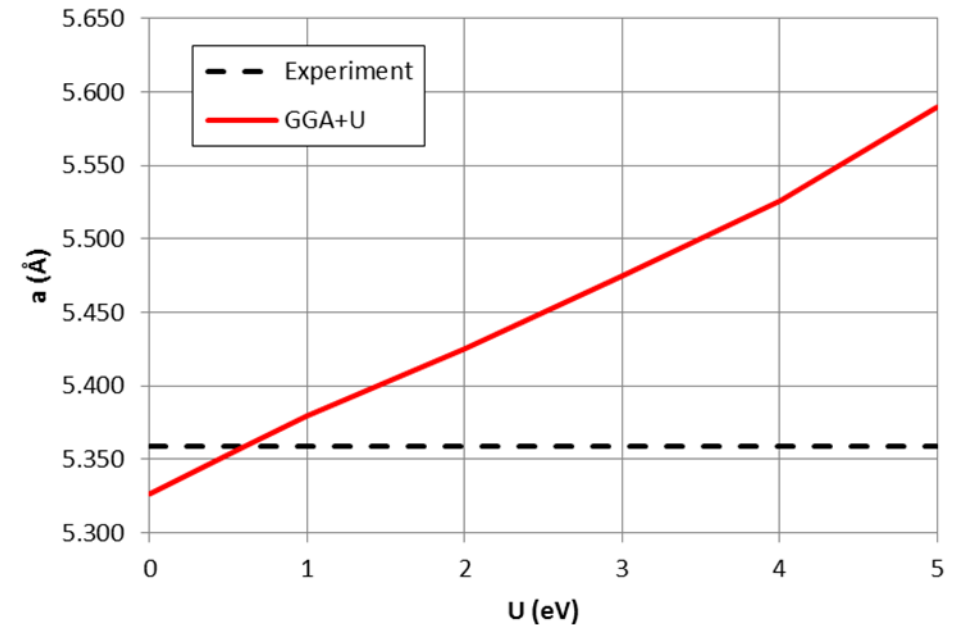
VASP structure optimization of PuH$_2$ using GGA+U.

PuH$_2$ Lattice Dynamics

- LD calculations performed using PHONON
  - Interatomic forces calculated by VASP
  - 2×2×2 supercell (96 atoms)
  - ±0.02 Å atom displacements
  - 0.02 Å^{-1} *k*-point spacing
    (3×3×3 *k*-point mesh)

- Dispersion relations (at right)
  - Well separated acoustic and optical modes
  - Lower branches are acoustic modes mainly due to heavy Pu atom vibrations
  - Higher branches are optical modes mainly due to light H atom vibrations

- Phonon DOS (next slide)

- No published INS measurements are available to verify calculated dispersion relations & phonon DOS
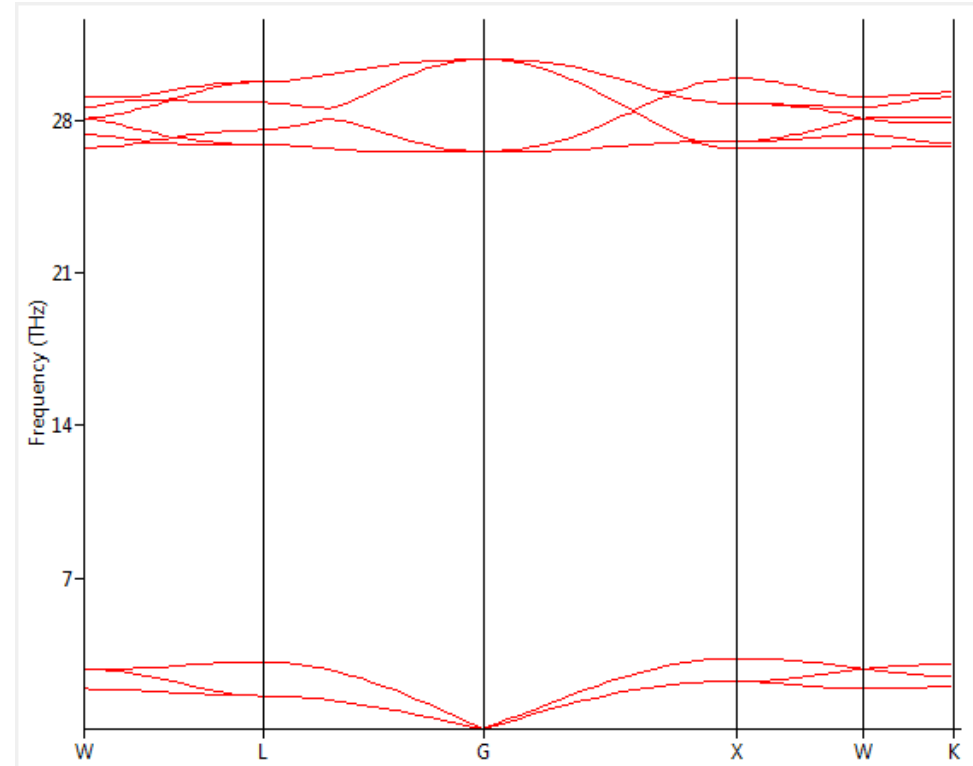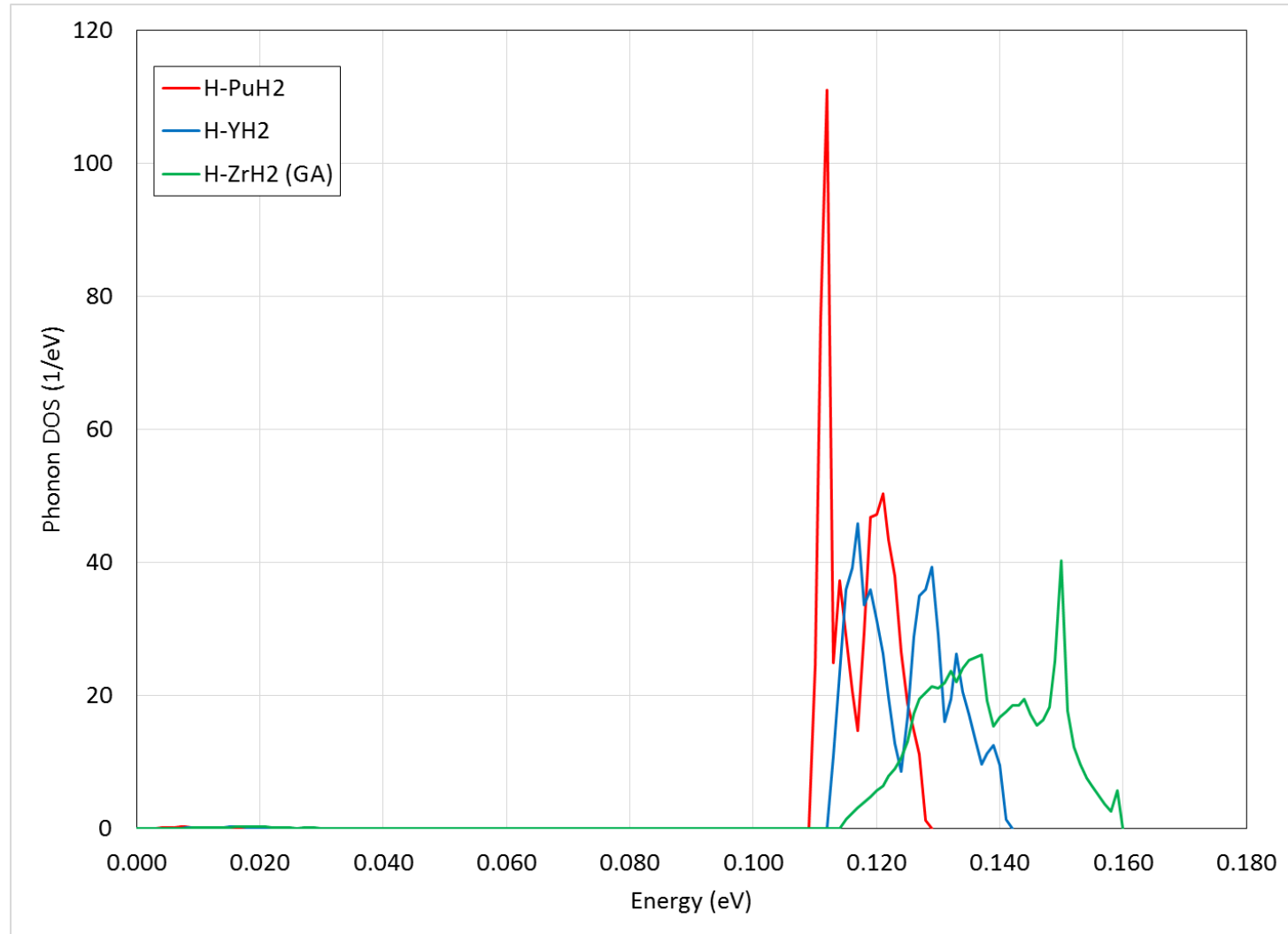

Calculated dispersion relation for PuH$_2$ along the highest-symmetry points of the Brillouin zone.

Calculated Phonon DOS for PuH$_2$
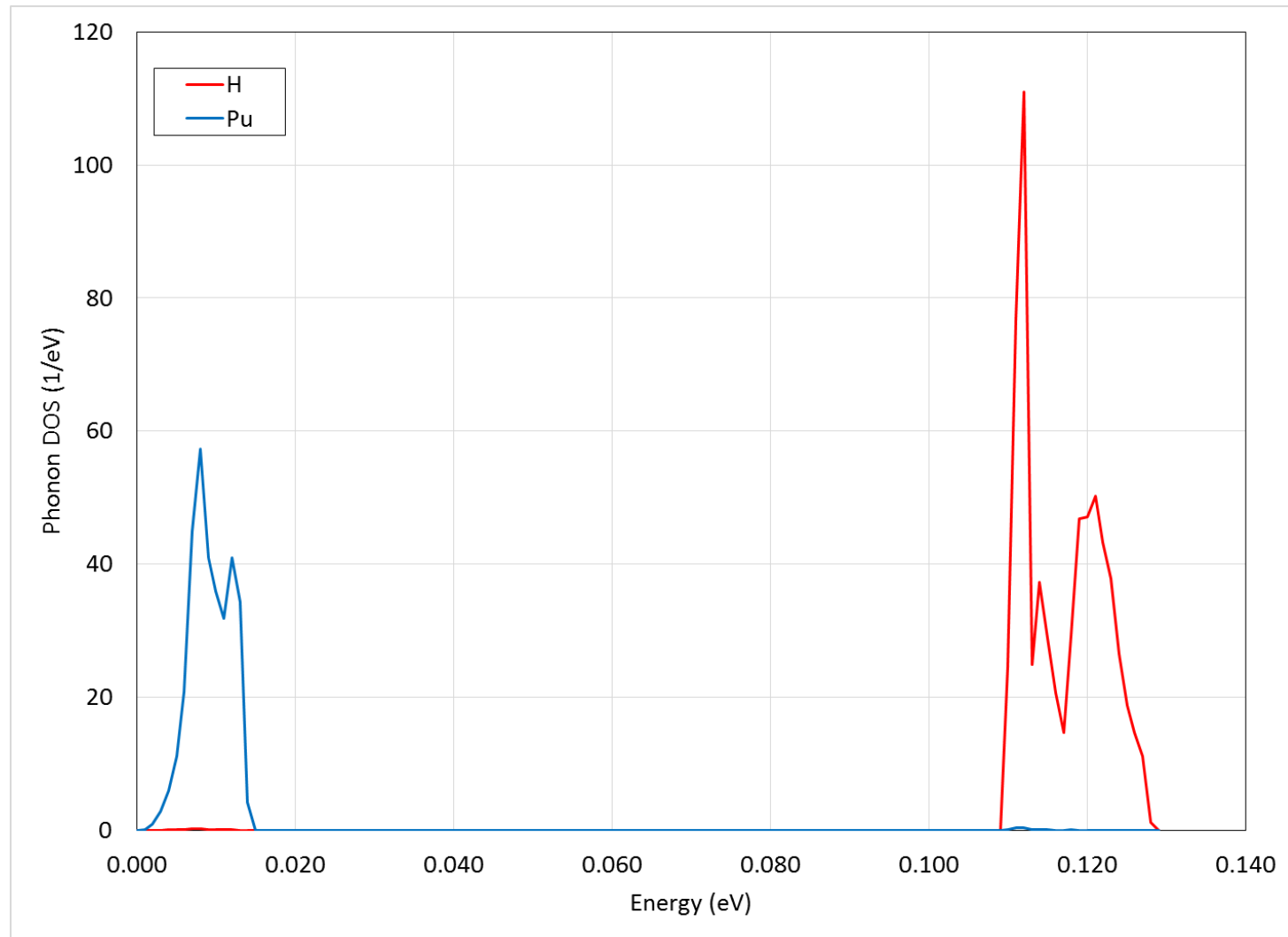
# Comparision of H Phonon DOS for Several Metal Hydrides

H-PuH$_2$ TSL Evaluation

- H-PuH$_2$ TSL generated using NJOY/LEAPR
  - H-PuH$_2$ phonon DOS from PHONON calculation
  - Incoherent approximation
  - Atomic mass ratio and free atom scattering cross section for ^{1}H from ENDF/B-VII.1
  - α and β grids optimized to treat scattering up to 5 eV without SCT approximation
  - Temperature evaluated at 293.6 K (room temp.)

- Pu-PuH$_2$ TSL not evaluated at this time
  - LEAPR can't properly treat Pu coherent elastic scattering in PuH$_2$ without extensive modifications
  - Deferring evaluation of Pu-PuH$_2$ until beta2 version of FLASSH code is available (expected Fall 2017)
    - Proper treatment of coherent elastic scattering and relax incoherent approximation

- Use free gas approximation for Pu
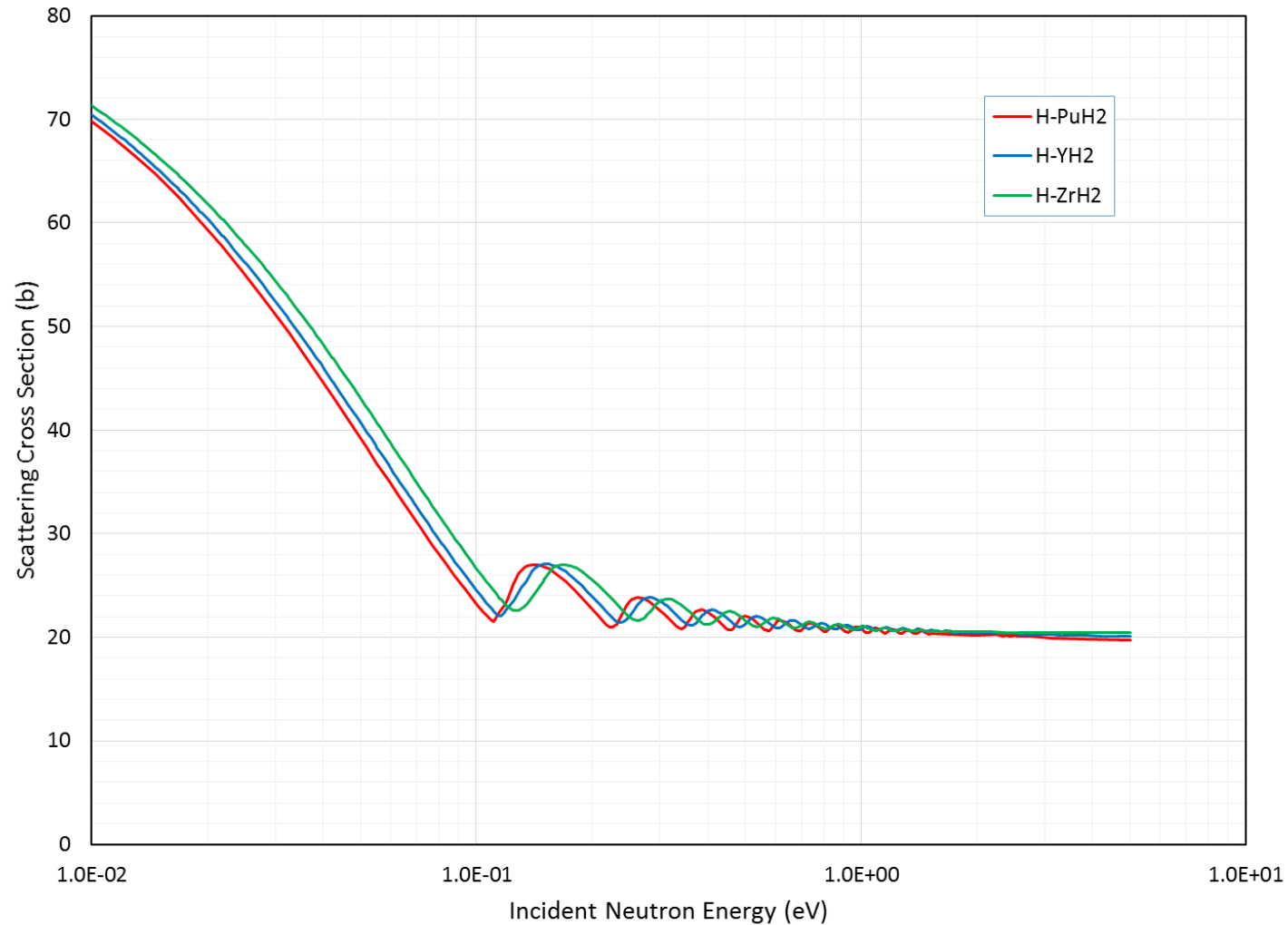 - Small approximation for PuH$_2$ since H scattering dominates
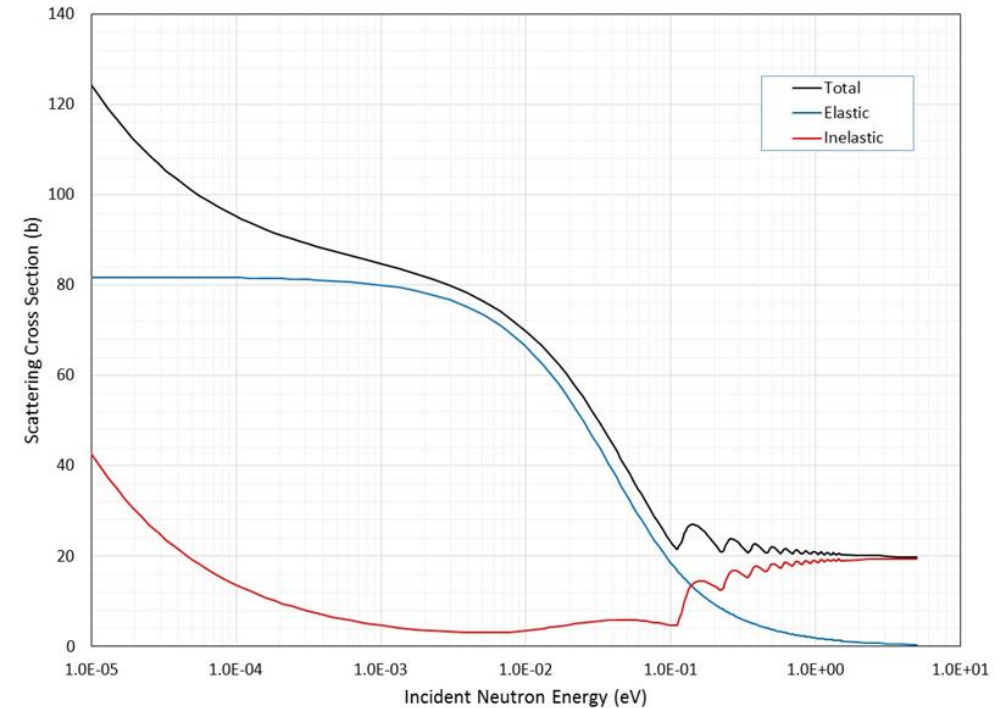
Total, elastic, and inelastic scattering cross section for H-PuH$_2$ at 293.6 K generated by NDEX

Comparision of Total Scattering Cross Sections for H-PuH$_2$, H-YH$_2$, and H-ZrH$_2$
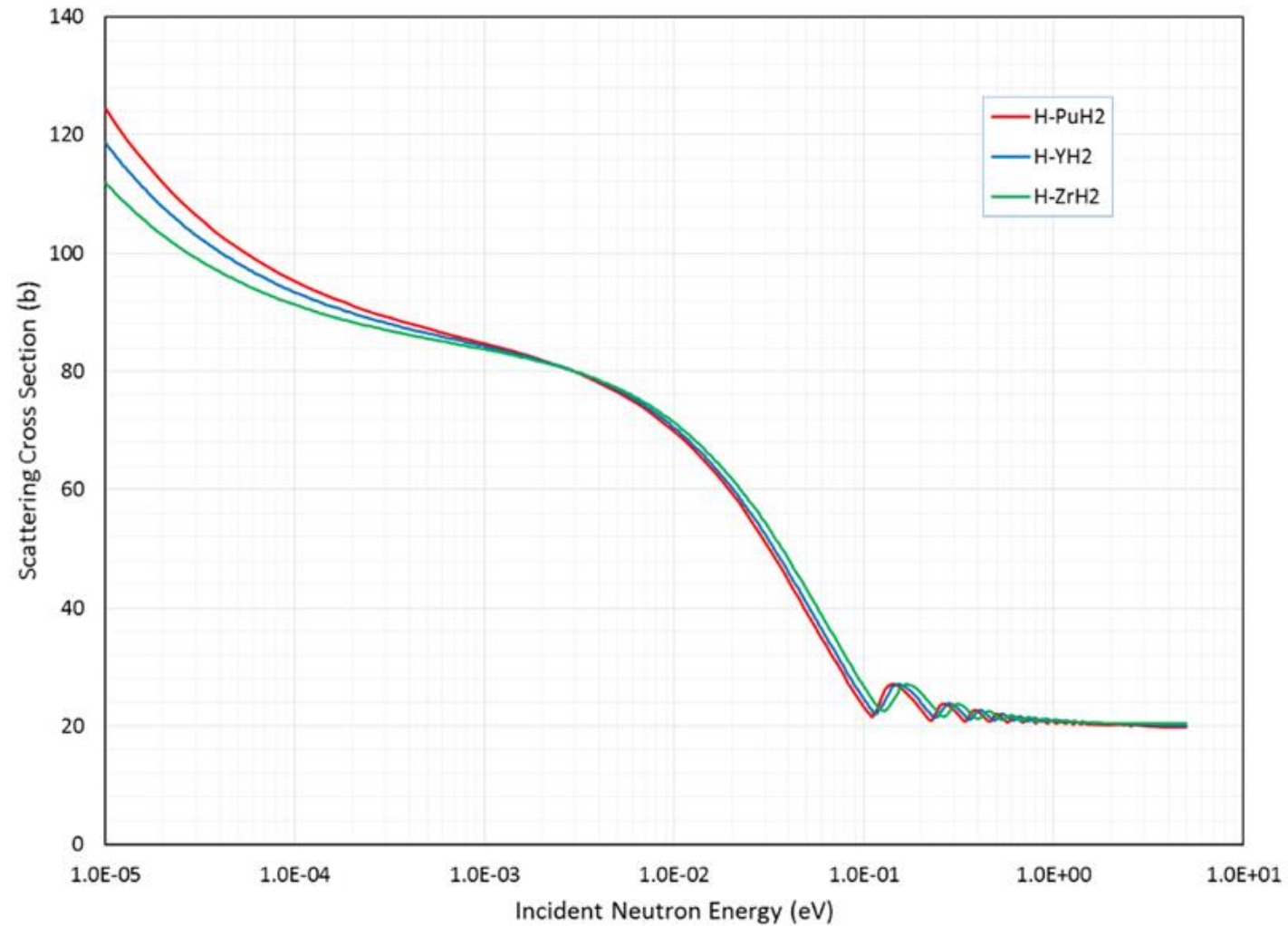
Comparision of Total Scattering Cross Sections for H-PuH$_2$, H-YH$_2$, and H-ZrH$_2$

Calculated Critical Mass

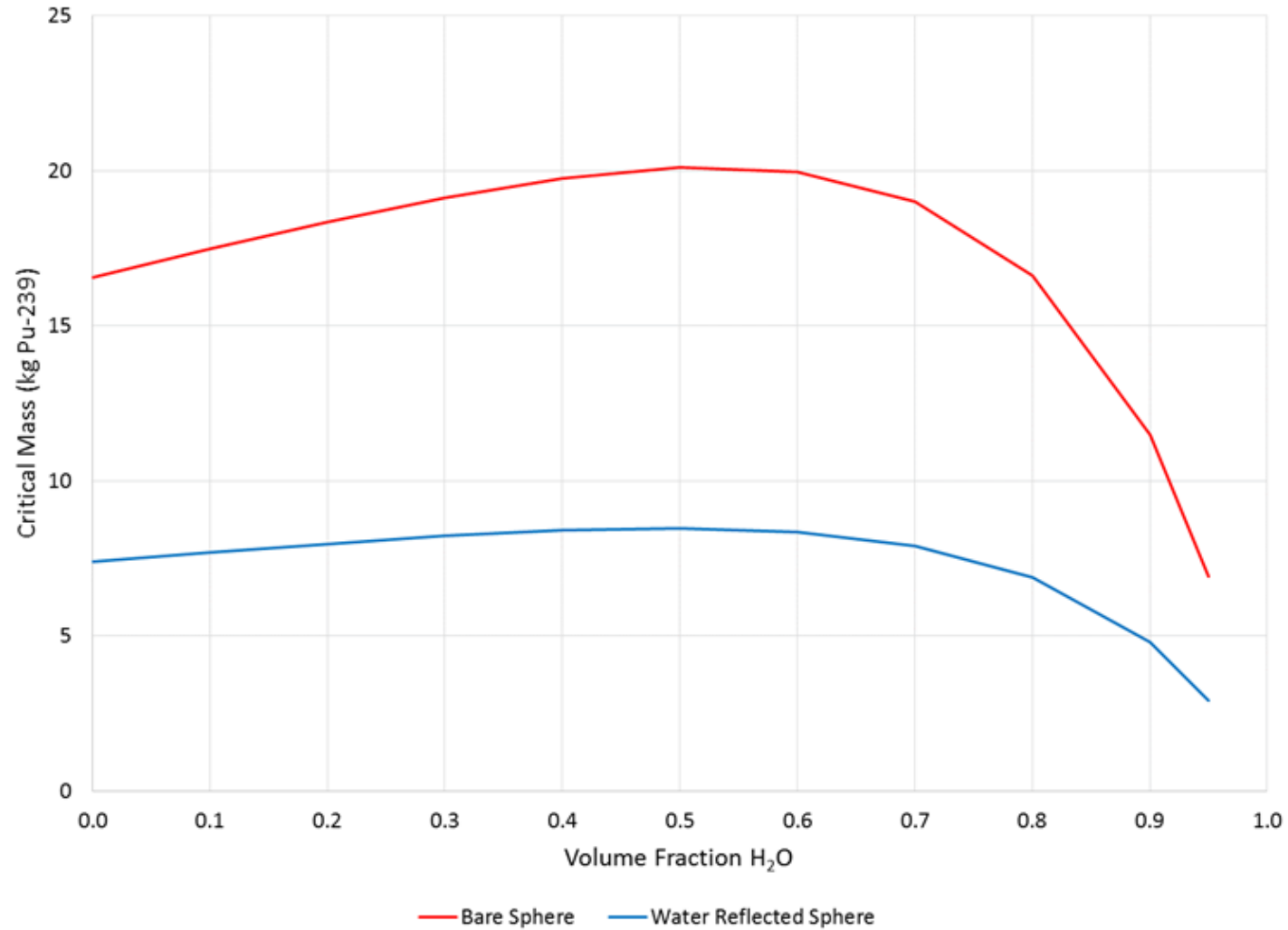- Calculated critical mass
  - Bare sphere
  - Water-reflected (20 cm thick) sphere
  - Solid 239PuH$_2$ core
  - Moderated ^{239}PuH$_2$ + H$_2$O slurry core
    - 0.0-0.95 H$_2$O volume fraction
    - 2 – 51 H/^{239}Pu ratio

- Codes and cross sections
  - MC21 v8.0.0 – Monte Carlo
  - NDEX v8.0.0 – ND processing
  - ENDF/B-VII.1 cross sections @ 293.6 K

- ^{239}PuH$_2$ + H$_2$O core modeling details
  - Homogenized slurry
  - H-PuH$_2$ TSL
  - H-H$_2$O TSL
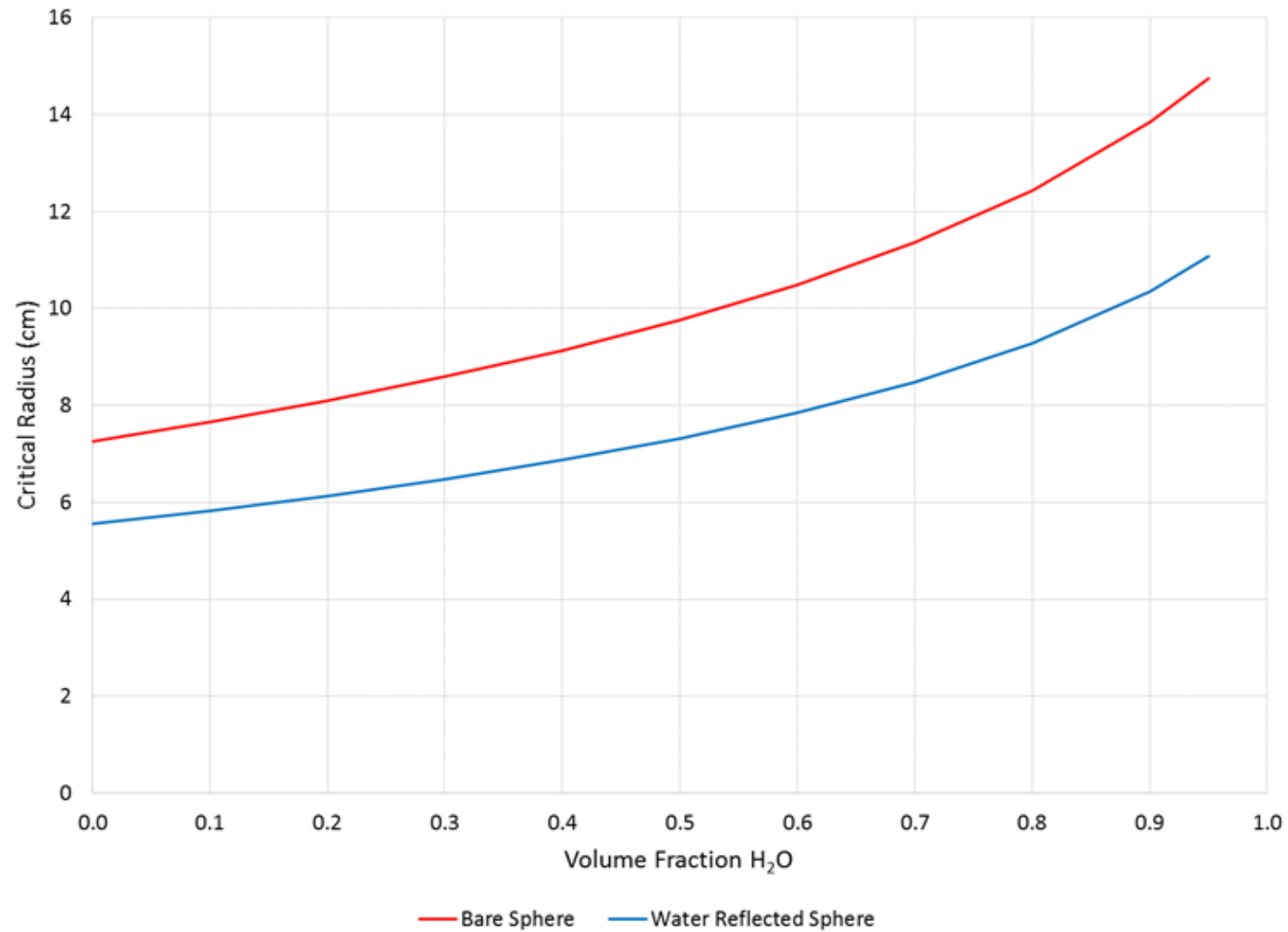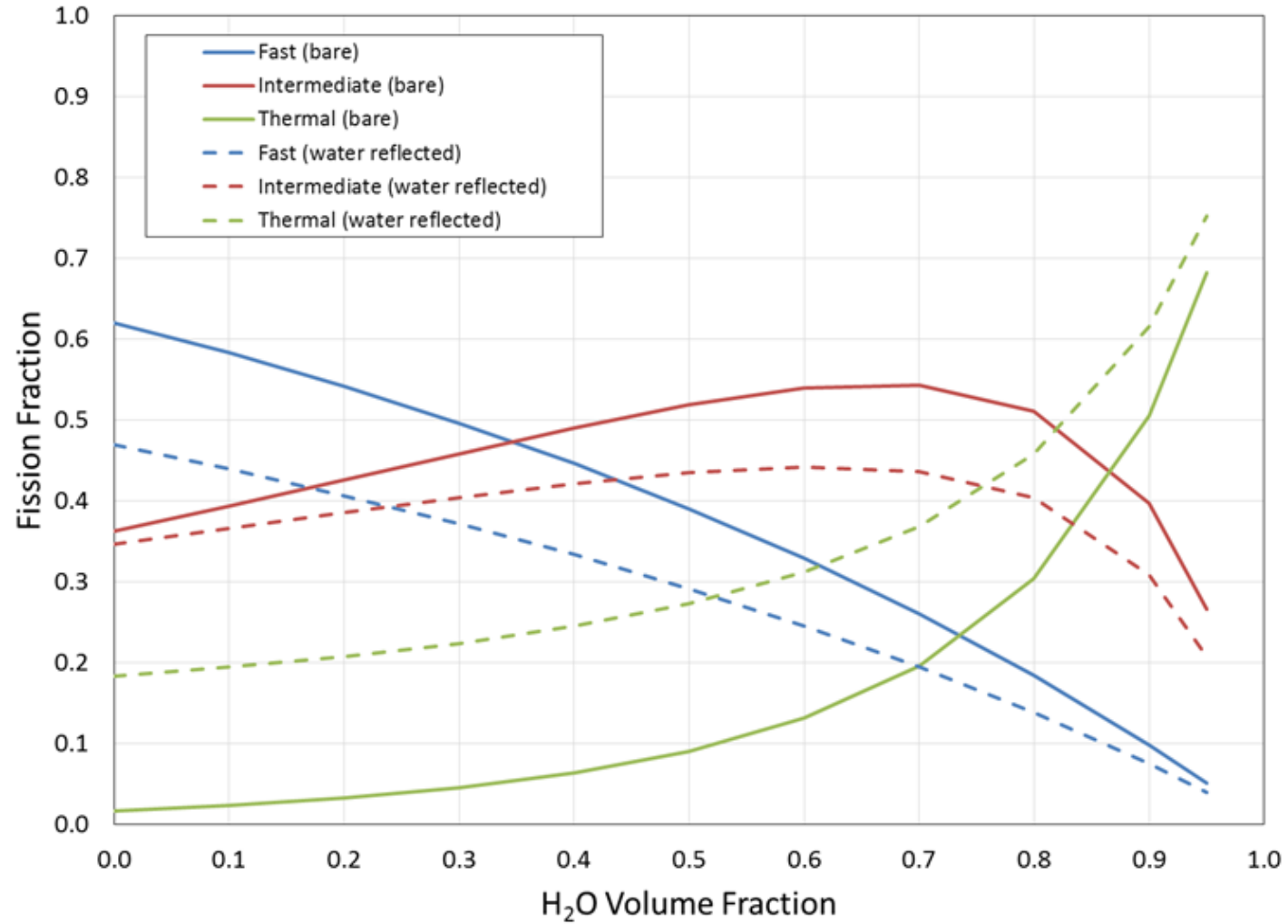 - ^{239}Pu free gas
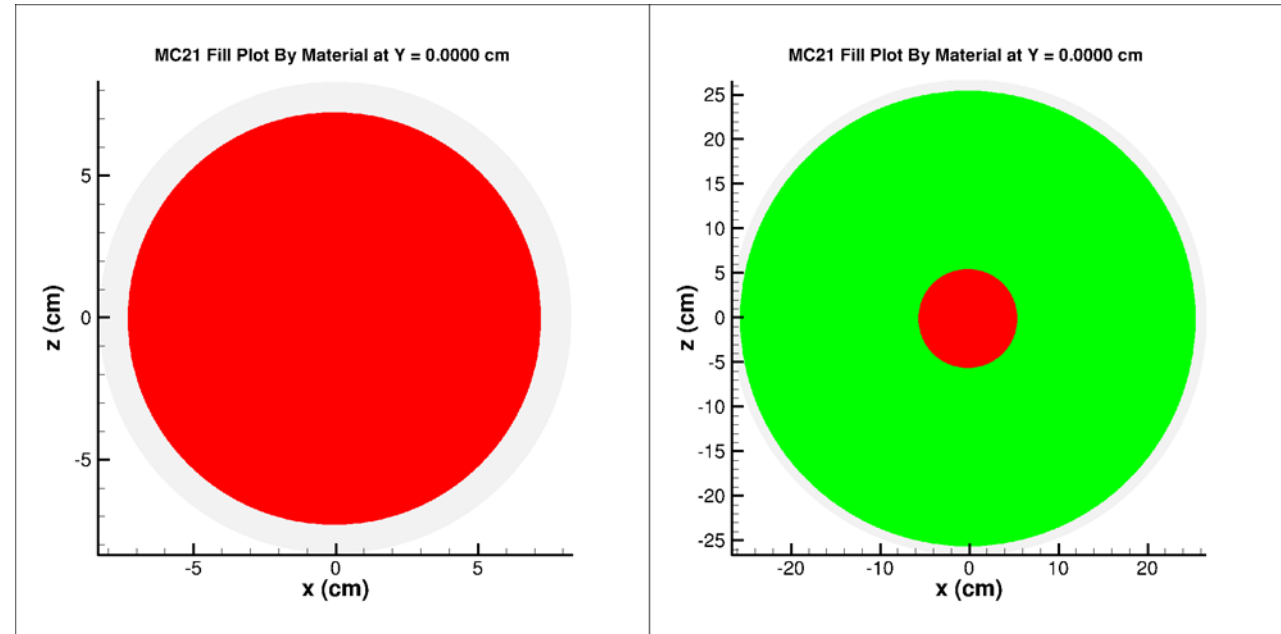
Bare Sphere   Water-reflected Sphere
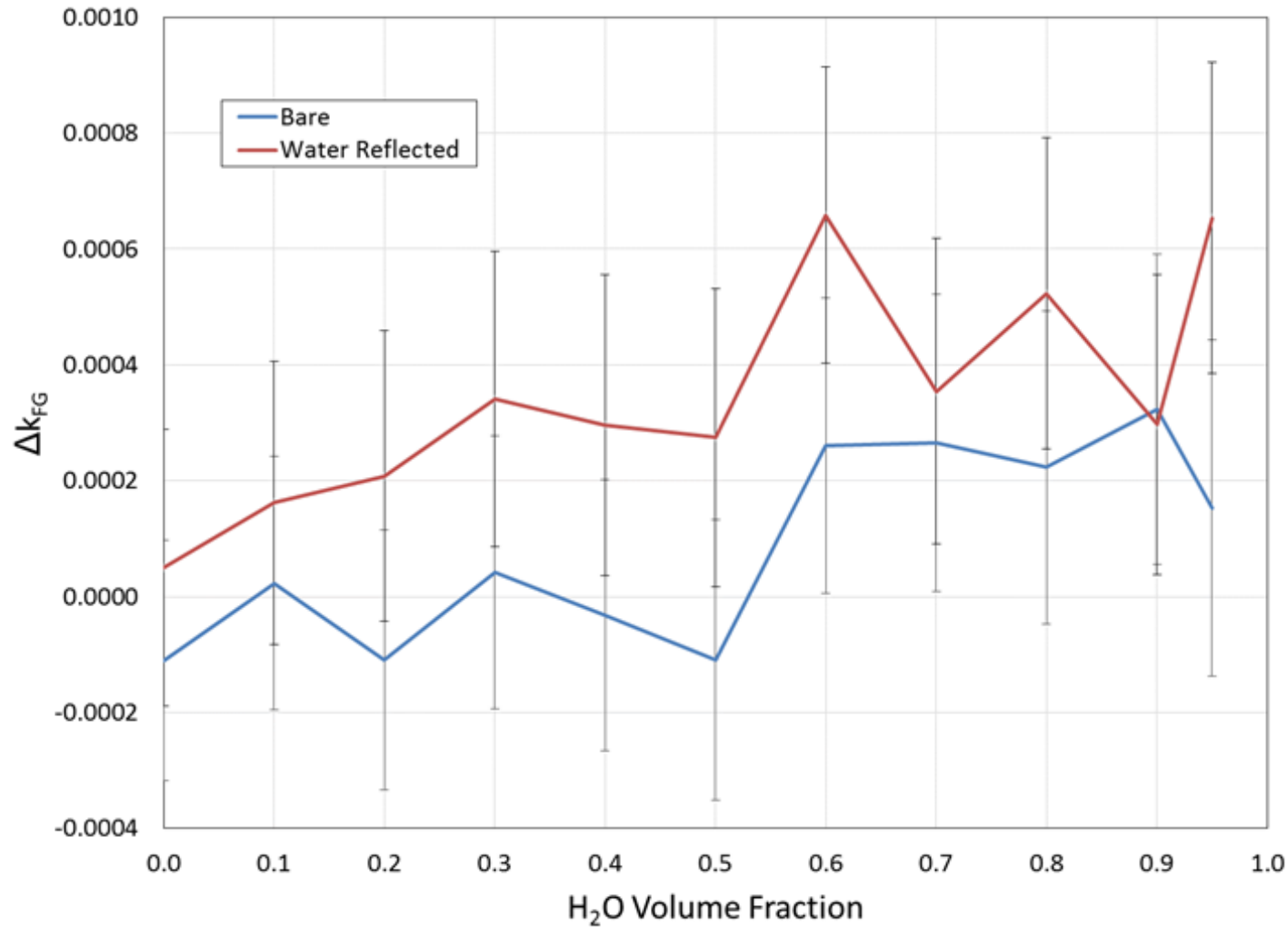
Calculated Critical Mass

Calculated Critical Radius

Fission Fractions for Bare and Water-Reflected Cases

Difference in k_{eff} between ^{1}H free-gas and H-PuH$_2$ TSL Treatments
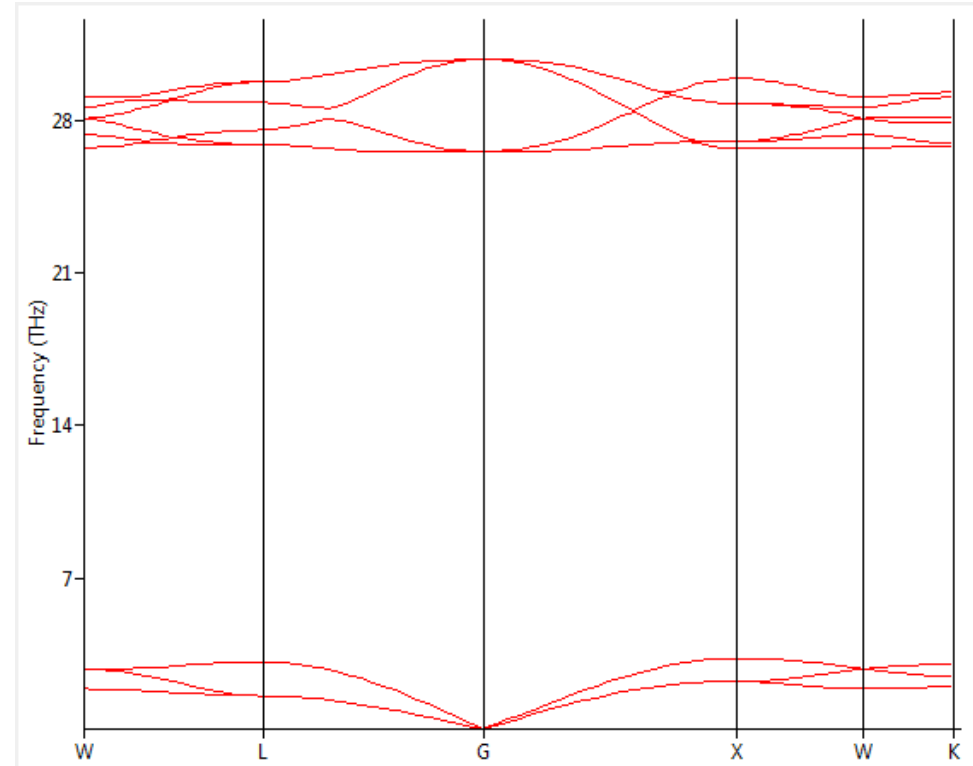

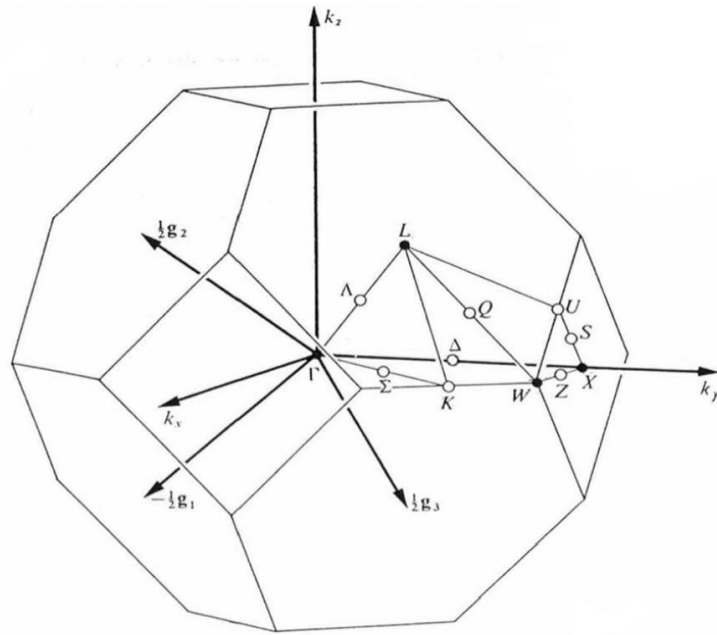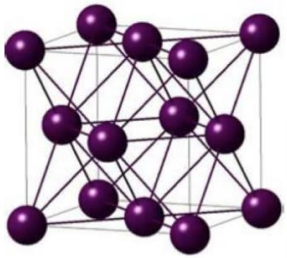Error bars provide 95% CI on Δk

Conclusions

- TSL for H-PuH$_2$ developed from first-principles DFT/LD calculations
- Suitable for analysis of bulk PuH$_x$ composition with $0.0 < x < 2.0$
- Predicted critical mass and radius provided for
  - Bare and water-reflected ^{239}PuH$_2$ sphere
  - Bare and water-reflected homogenized ^{239}PuH$_2$ + H$_2$O slurry
- H-PuH$_2$ TSL yields small reduction of k_{eff} for moderated configurations

- Lack of published inelastic neutron scattering data for PuH$_x$ impedes validation of TSL

Backup Slides

PuH$_2$ Lattice Dynamics

FCC Brillion Zone

Calculated dispersion relation for PuH$_2$ along the highest-symmetry points of the Brillouin zone.