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Title:	Multiphase Uranium EOS
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Form 836 (7/06)

Multiphase Uranium EOS

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We present the results of an empirically derived multiphase Uranium equation of state. The equation of state includes the orthorhombic, bcc and fluid phases. The effects of phase transitions (Clausius-Clayperon, volume changes, specific heats) are treated self-consistently. We will also present comparisons of the equation of state to electronic structure results.

Multiphase Uranium EOS

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Acknowledge: Eric Chisolm

Introduction

- Each phase is constructed with its own Helmholtz free energy using conventional modeling techniques.
- The phase boundaries are calculated by matching the Gibbs free energy.
- Each phase represents the minimum of the Gibbs free energy.
- All phases have been constrained to the available data, α-U in particular.

Three-term Decomposition of Free Energy

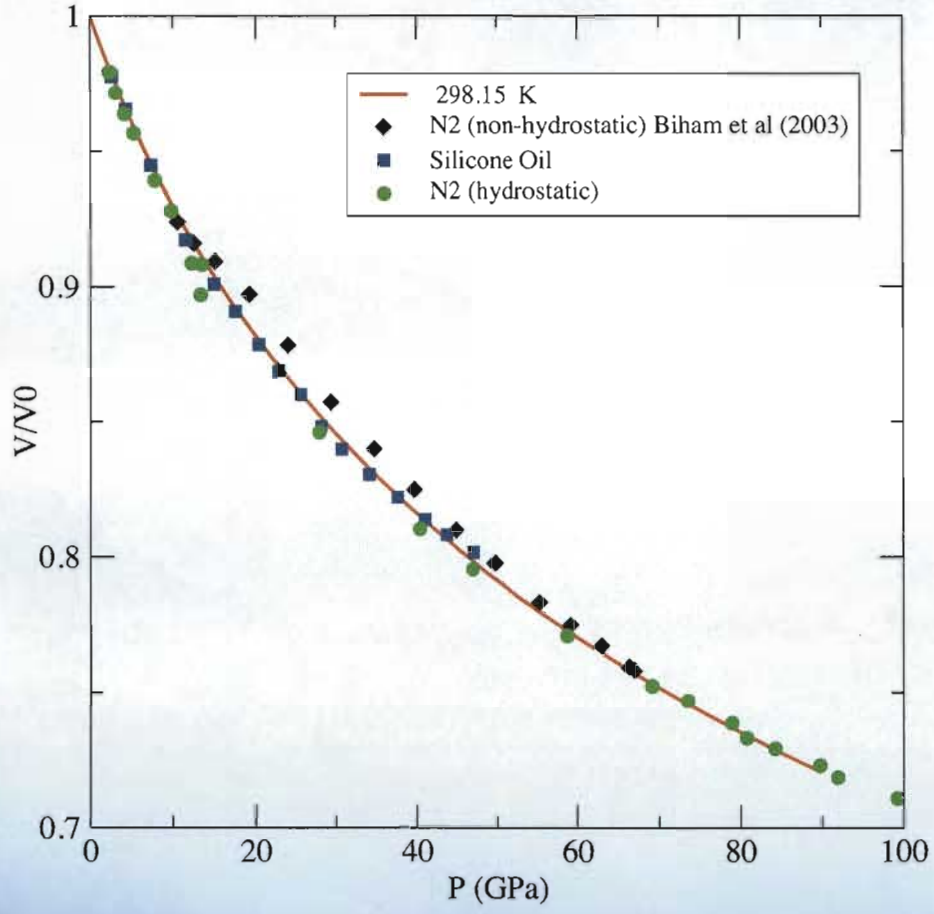
- We express the Helmholtz free energy as:

$$F(V,T) = \phi_0(V) + F_{\text{ion}}(V,T) + F_{\text{el}}(V,T)$$

$\phi_0(V)$	cold curve contribution (Rose analytic form)
$F_{\text{ion}}(V,T)$	cold + thermal ionic contribution (Debye model with a correction for liquid)
$F_{\text{el}}(V,T)$	thermal electronic contribution (Linear specific heat)

Questions: Is this free energy too simple? Should we include anharmonic, electron-phonon and/or a more complicated electronic part?

Alpha Phase Uranium
Room Temperature Comparison to Select DAC Data



Imposed Model Constraints/Assumptions

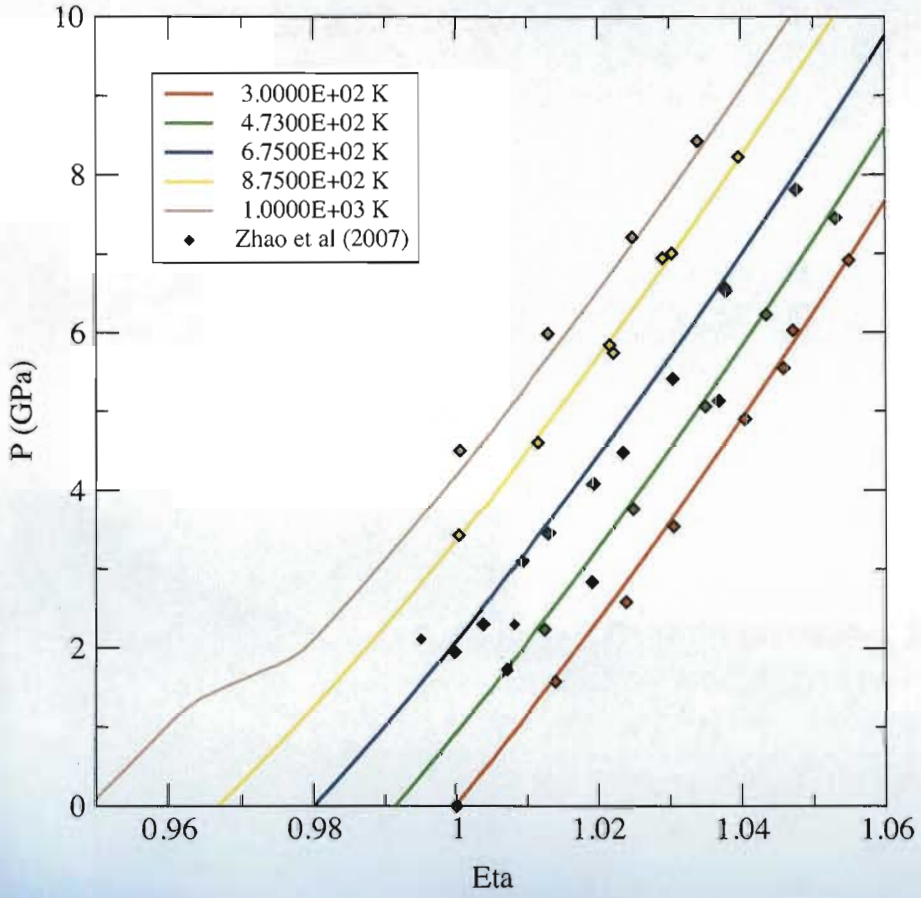
- B_s, dB_s/dP
- ρ_{ref}

Analytic cold curve is adjusted to match data

- B_s = 114.5 GPa
- B' = 5.7
- B_T = 111.0 GPa
- ρ_{ref} = 19.0429 g/cc

T. LE BIHAN et al., Phys. Rev. B 67, 134102 (2003)

Alpha Phase Uranium
Comparison to Static Compression Diffraction Data



Imposed Model Constraints/Assumptions

- B_s, dB_s/dP
- ρ_{ref}

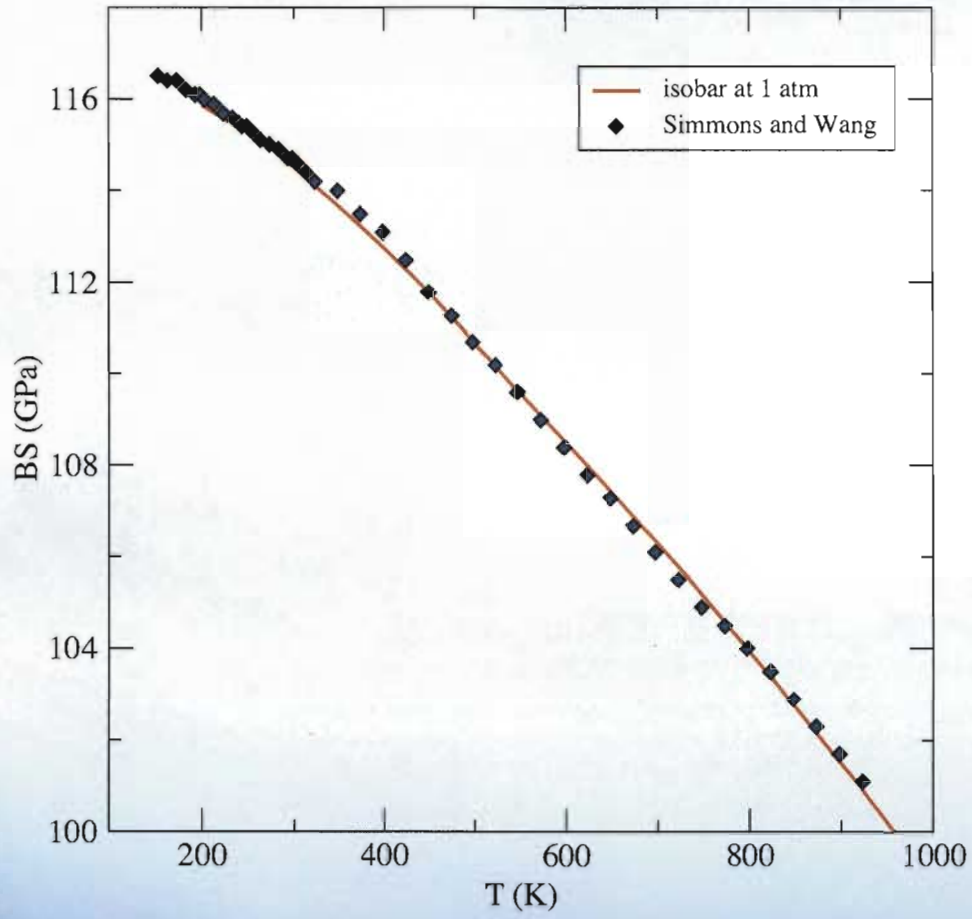
Validates choice for the following

$$\gamma = \frac{\alpha B_s V}{C_p} = 2.16$$

$$\frac{d\gamma}{d\ln\rho}$$ is small

ZHAO *et al.* Phys. Rev. B **75**, 174104 (2007)

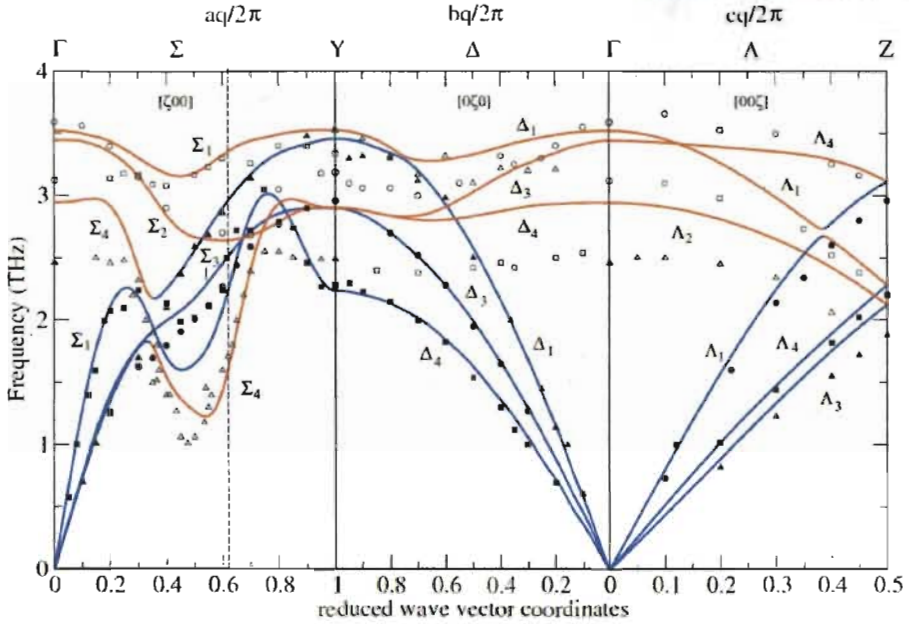
Alpha Phase Uranium
Comparison to Thermal Dependence of Bulk Moduli Data



Imposed Model Constraints/Assumptions

- B_s, dB_s/dP
- ρ_{ref}
- Γ – linear specific heat coefficient

Alpha Phase Uranium
Phonons and Thermodynamics

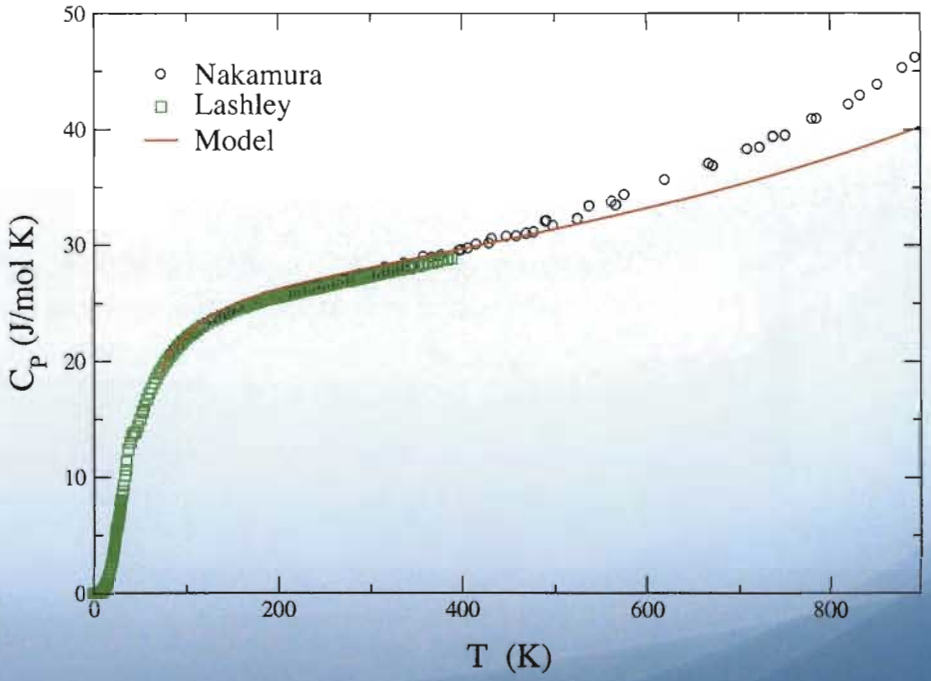


DFT calculation of α-U phonon dispersion by J. Bouchet, PRB 77 2008, generally agrees well with experiment.

Gives effective Debye T, θ_2=168 K.

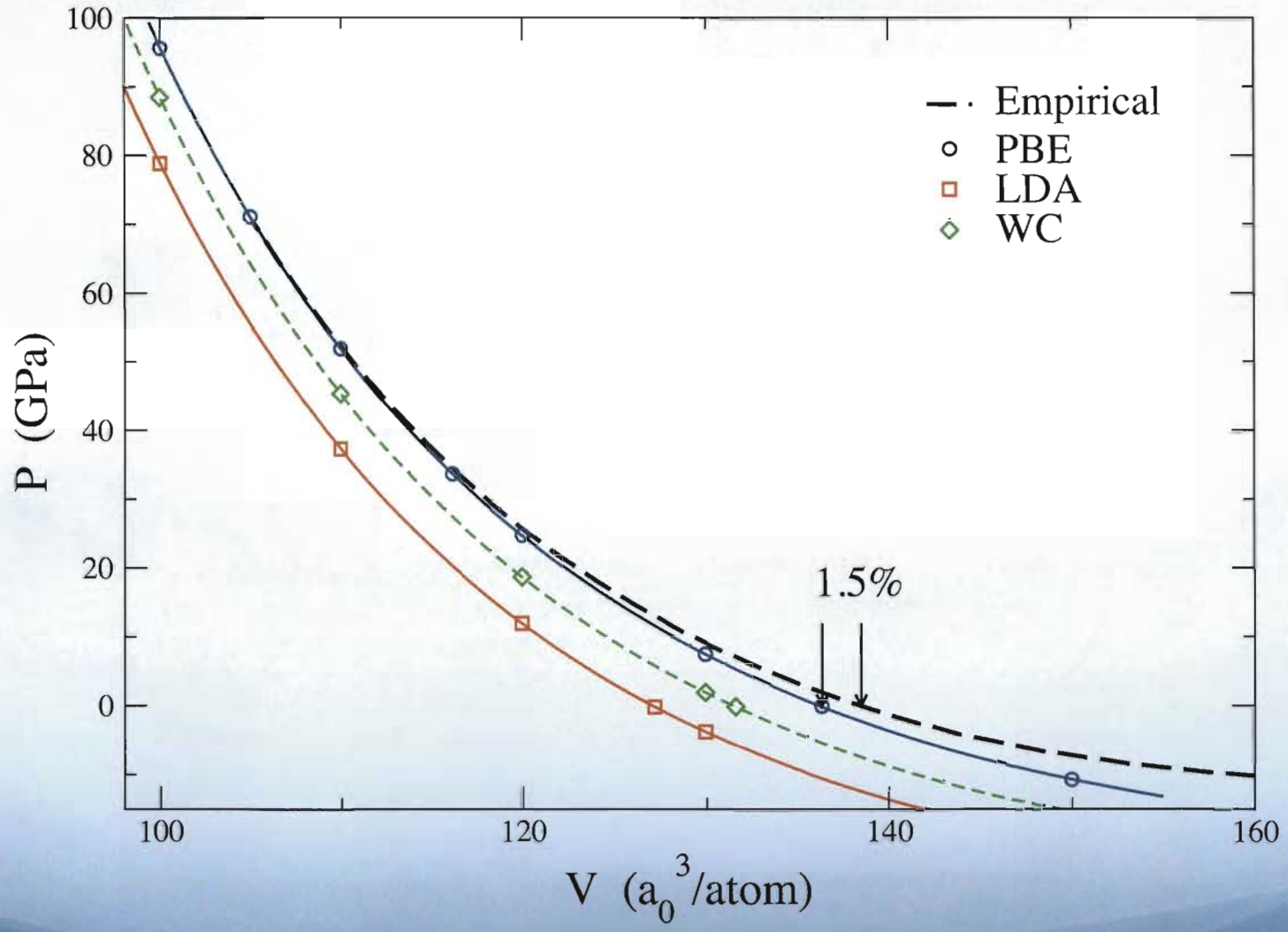
Empirical model based on specific heat, entropy.

Debye T, θ=173 K.



Cold Pressure – Empirical vs. DFT

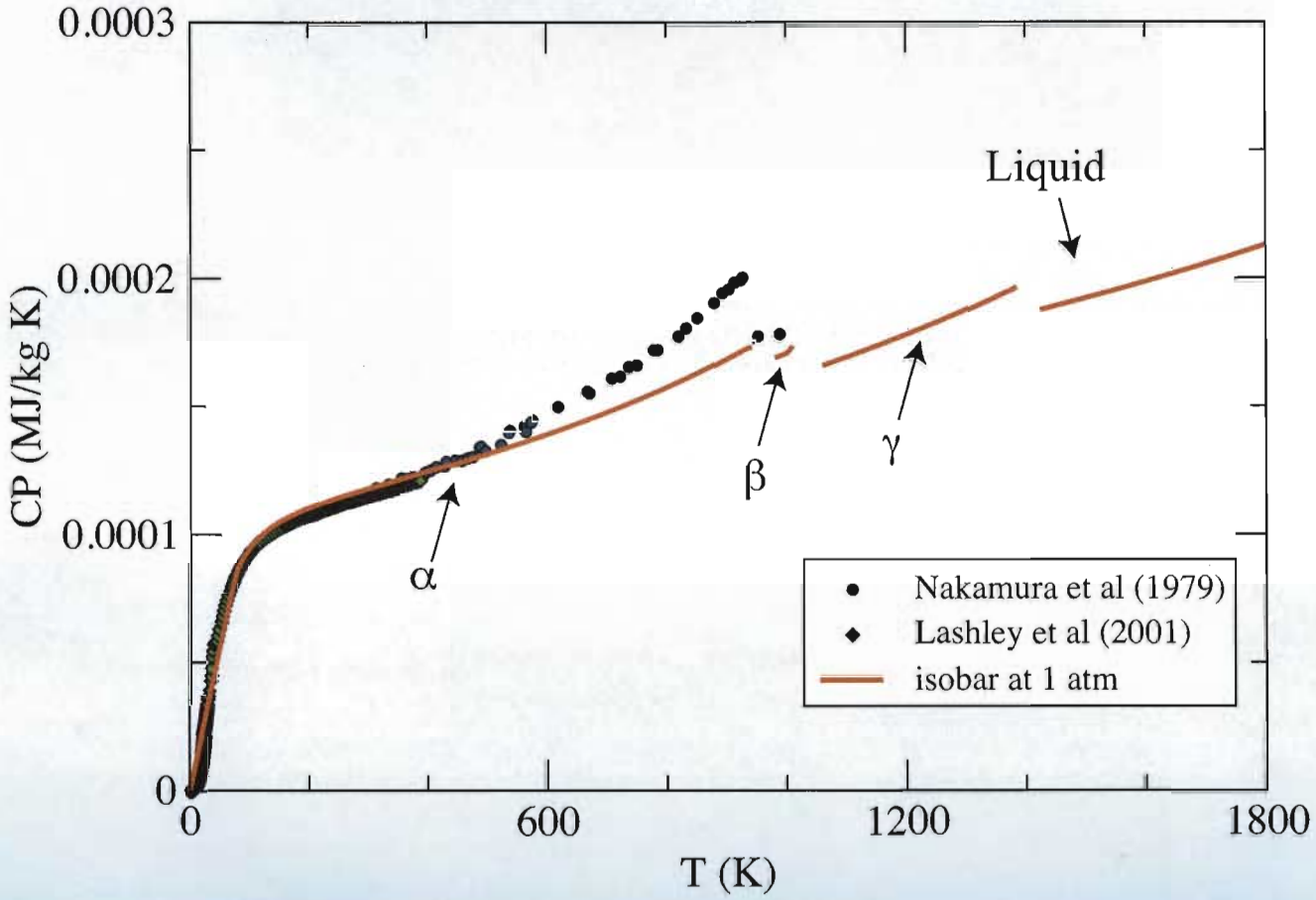
DFT provided by Carl Greeff



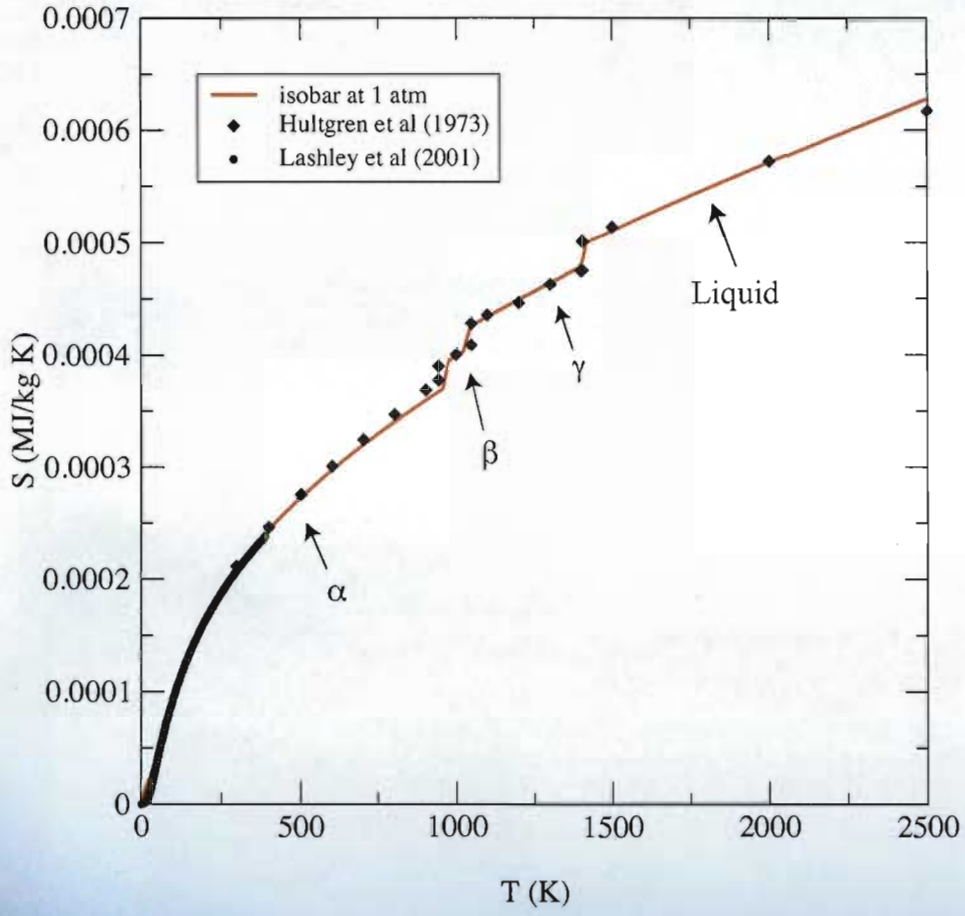
Alpha Phase Uranium

- Alpha Phase
  - Appears to match data
  - Agrees well with DFT
- Next Steps
  - Constrain other phases to available data and bind the phases together using phase boundary data
  - Phase transitions are treated self-consistently (Clausius-Clayperon, volume changes, specific heats)

Multiphase Uranium
Comparison to Specific Heat Data



Multiphase Uranium
Comparison to Entropy Data



Imposed Model Constraints/Assumptions

Relative values of:

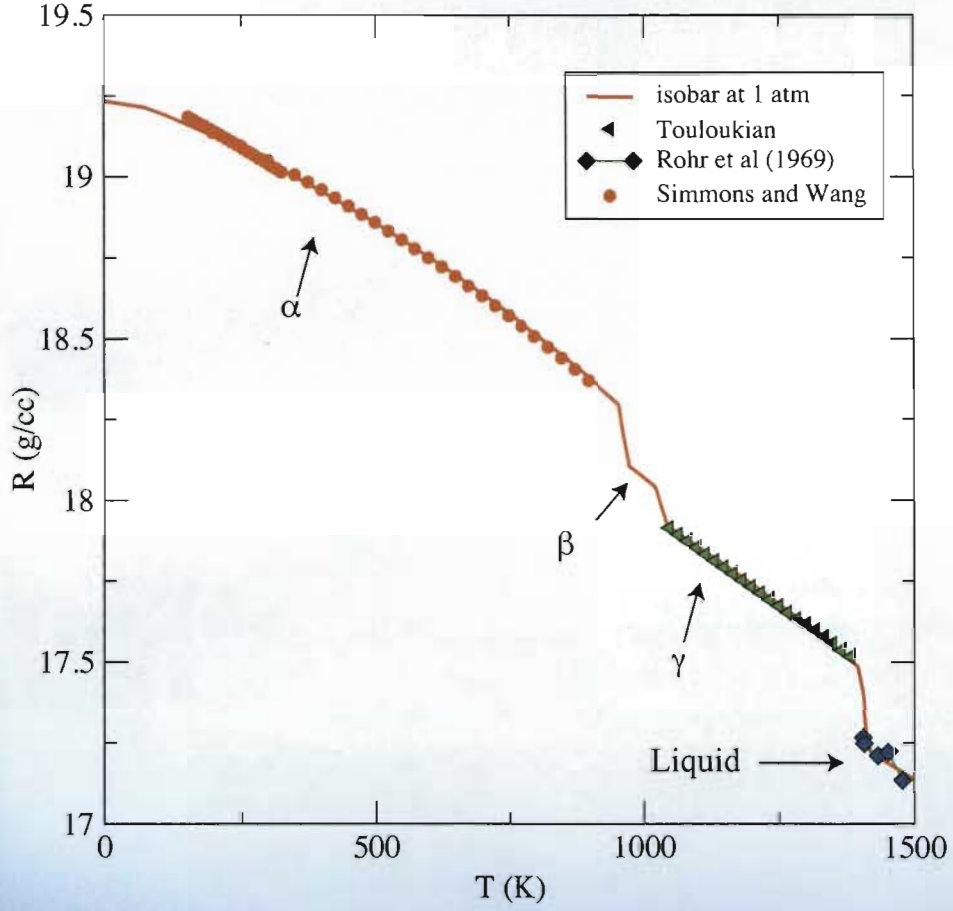
- θ_{Debye}
- γ

The ratios of the various θ_{Debye} for each phase are set to match the data.

Entropy difference between the phase are:

$\alpha - \beta$	$(\Delta S)_P \approx 0.617\ k_B$/atom
$\beta - \gamma$	$(\Delta S)_P \approx 0.514\ k_B$/atom
γ – Liquid	$(\Delta S)_P \approx 0.526\ k_B$/atom

Multiphase Uranium
Comparison to Density vs. Temperature Data



Imposed Model Constraints/Assumptions

Relative values of:

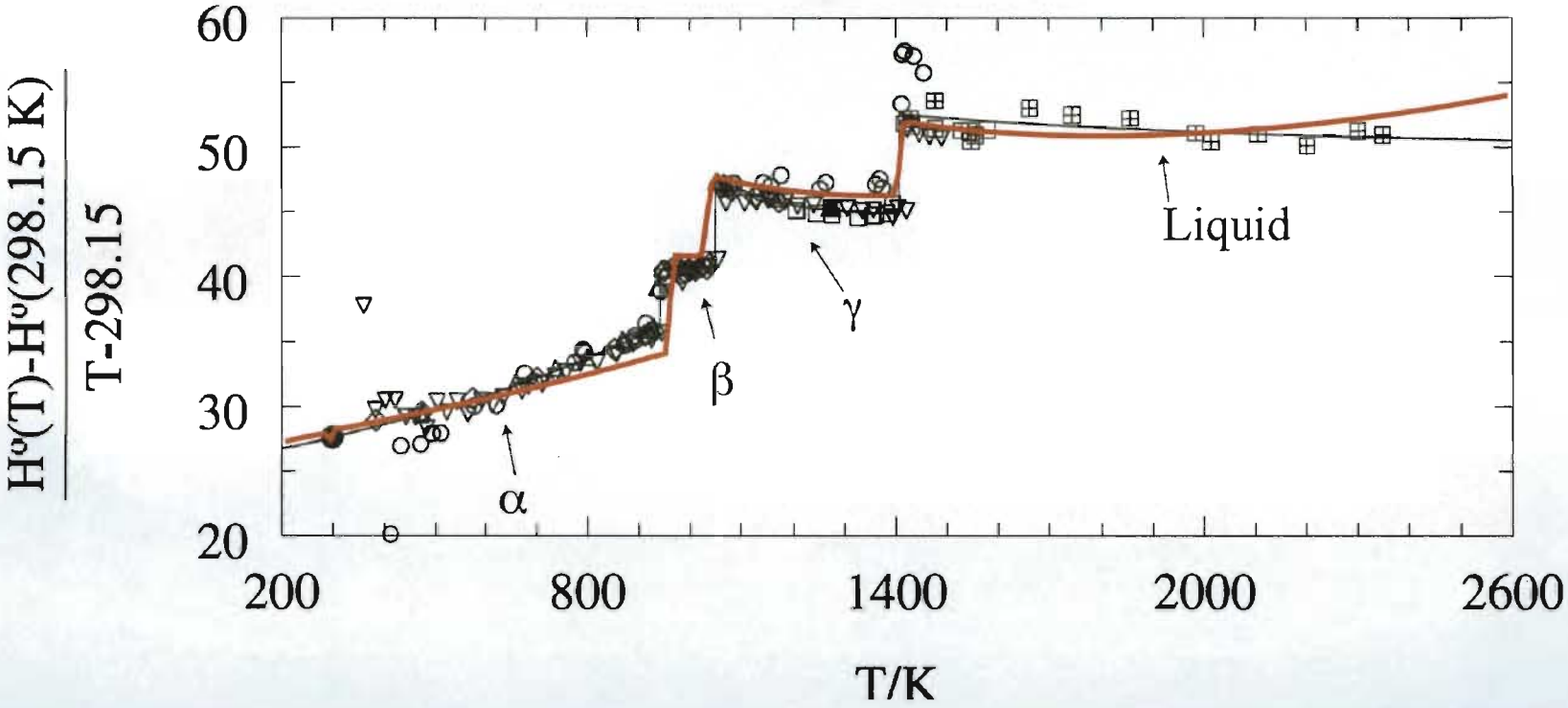
- ρ_{ref}
- γ

The densities for each phase are set to match the data.

Density percent difference between the phase are:

$\alpha - \beta$	0.92 % @ 941 K
$\beta - \gamma$	0.59 % @ 1051 K
γ – Liquid	1.36 % @ 1408 K

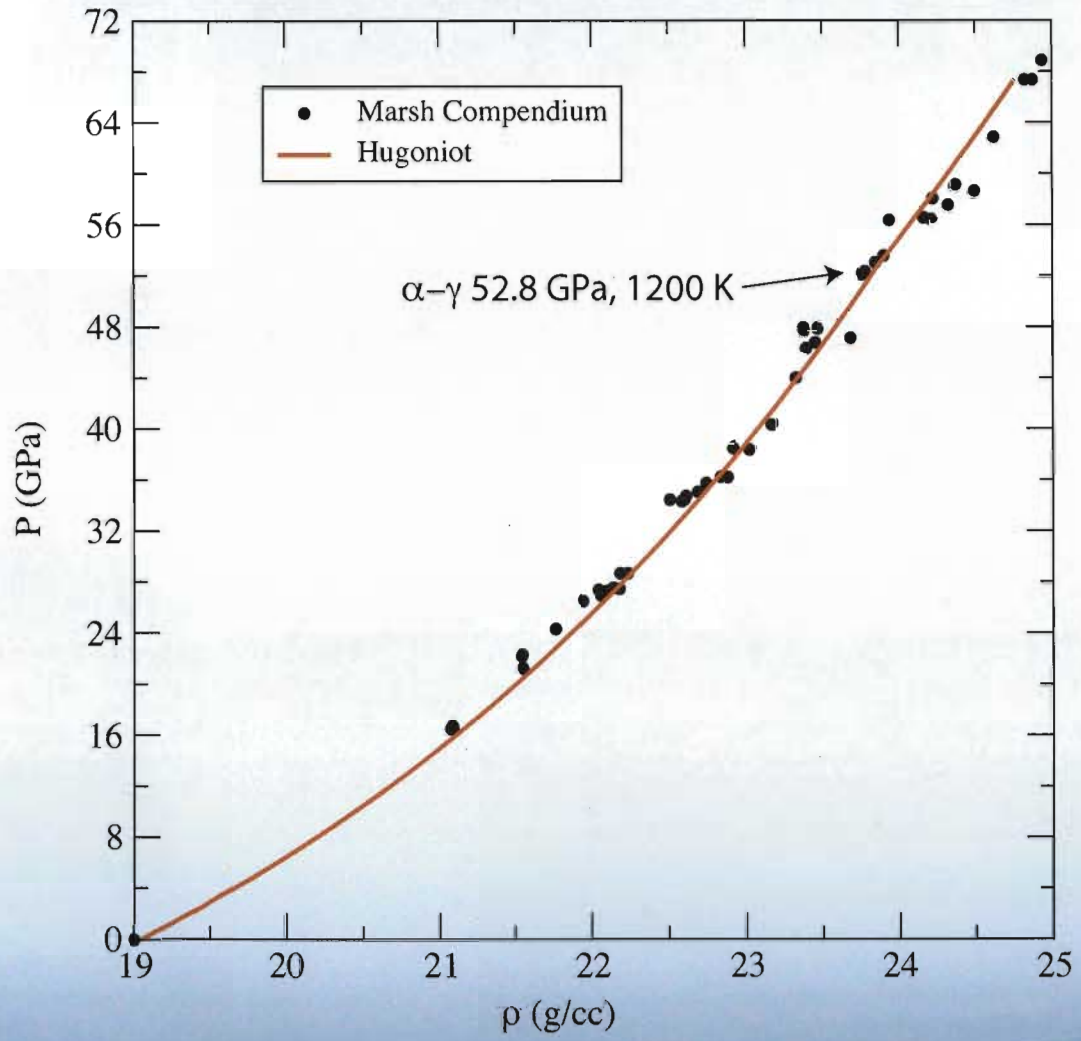
Multiphase Uranium
Comparison to Enthalpy Data



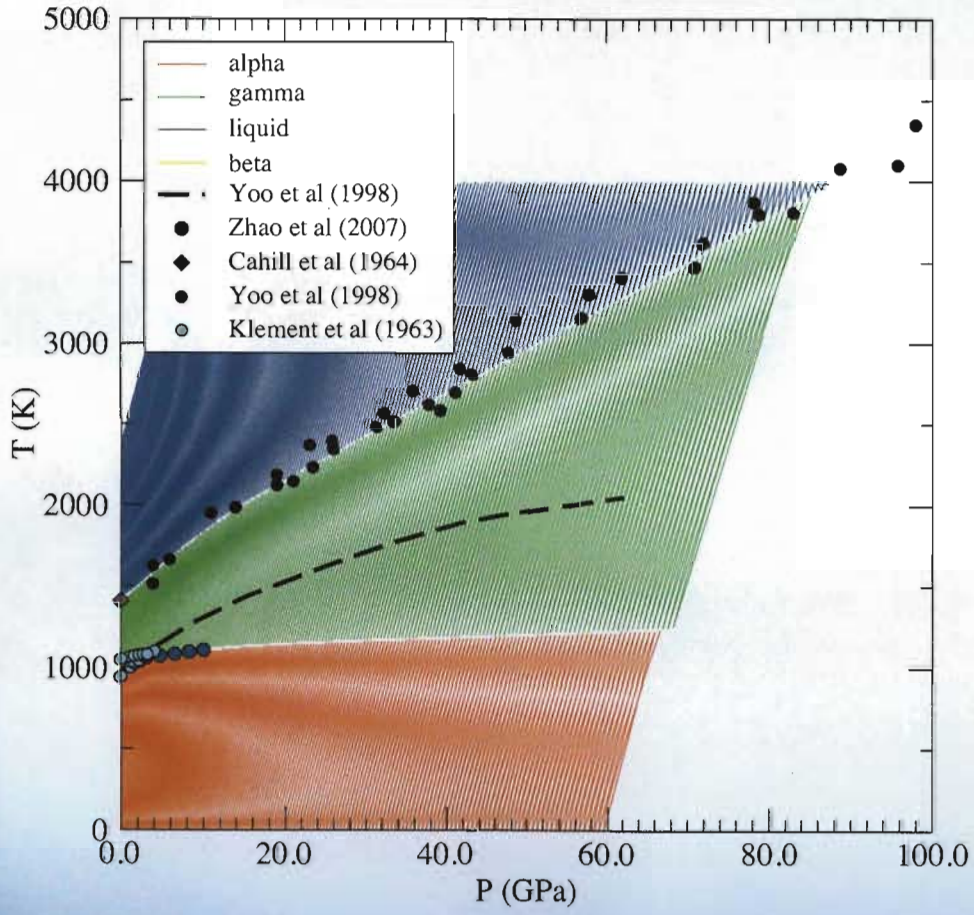
R. J. M. Konings and O. Benes, J. Phys. Chem. Ref. Data, Vol. 39, No. 4, 2010

Multiphase Uranium

Comparison to Shock Compression Data



Multiphase Uranium
Phase Diagram Compared to Data



Imposed Model Constraints/Assumptions

Relative values of:

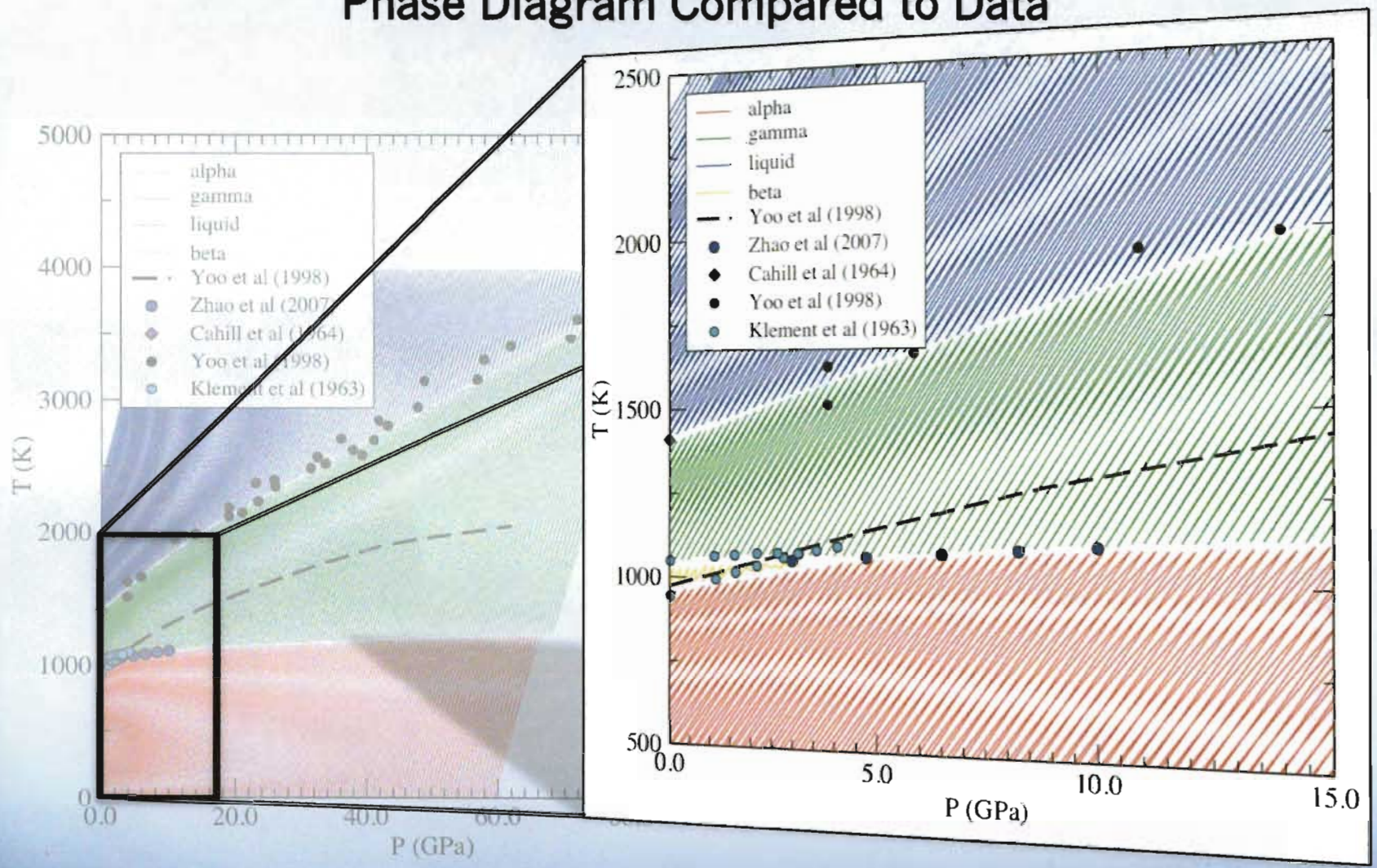
- E_0 – internal energy
- dB_s/dP

Constrained to:

$$\frac{dT}{dP} = \frac{\Delta V}{\Delta S}$$

Multiphase Uranium

Phase Diagram Compared to Data



Conclusions

- We have an excellent thermodynamically consistent representation of the four phases of Uranium.
- More experiments are needed to sample the phases at higher temperature and pressure.
- Would including the anharmonic, electron-phonon, and/or a more complicated electronic contribution to the free energy give us the correct C_P behavior?