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A New Wide-Range Equation of State for Xenon

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Session V6: Equation of State IV
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Sandia National Laboratories

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Overview

Part 1 — The Backstory:

Harmony between theory and experiment

Part 2 — The Journey:

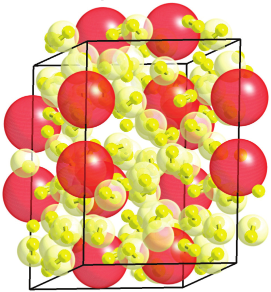
EOS model analysis and construction

Part 3 — The Results:

Comparing old and new EOS models with data

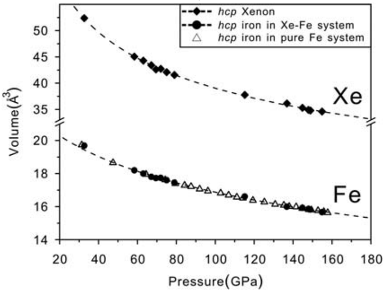
Xenon in compression

Novel compounds from DACs:



[Nature Chem. 2, 50 (2010)]

Planetary science:



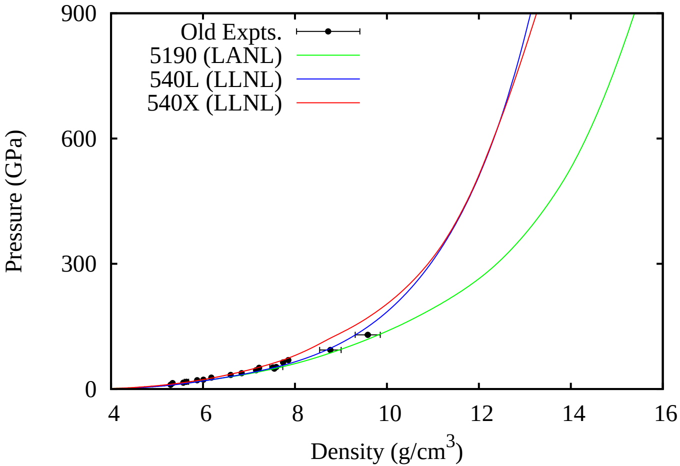
[Geophys. Res. Lett. 37, L04302 (2010)]

Limited high pressure data available:

- DAC compression/melting < 150 GPa
- First-principles cold curves < 700 GPa
- Liquid Hugoniot < 100 GPa

State of the EOS

Liquid xenon Hugoniot
($T_0 = 163$ K, $\rho_0 = 3$ g/cm^3)



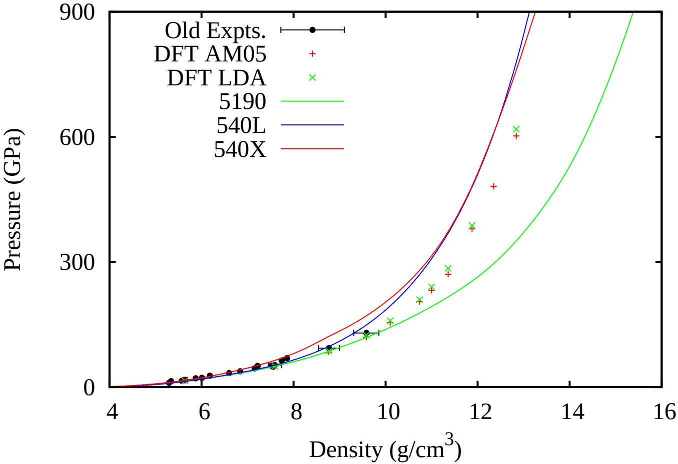
Large discrepancies between EOS models at high compression

Theory comes into play

CP1195, *Shock Compression of Condensed Matter - 2009*,
edited by M. L. Elert, W. T. Buttler, M. D. Furnish, W. W. Anderson, and W. G. Proud

DENSITY FUNCTIONAL THEORY (DFT) SIMULATIONS OF SHOCKED LIQUID XENON

Thomas R. Mattsson* and Rudolph J. Magyar†



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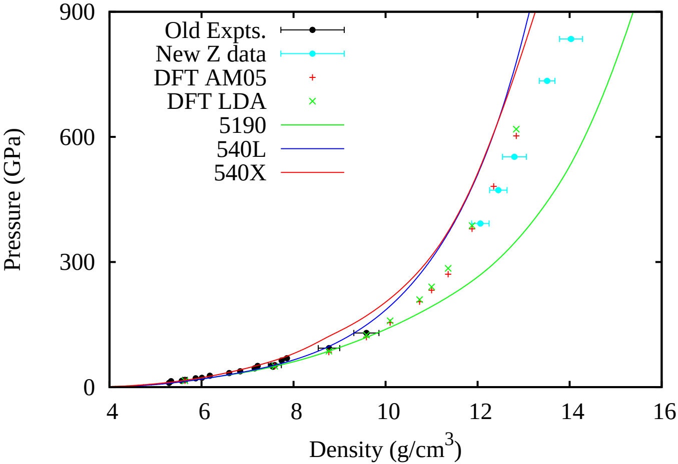
Time for experiments

PRL 105, 085501 (2010) PHYSICAL REVIEW LETTERS week ending 20 AUGUST 2010

Shock Compression of a Fifth Period Element: Liquid Xenon to 840 GPa

Seth Root,* Rudolph J. Magyar, John H. Carpenter, David L. Hanson, and Thomas R. Mattsson



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Part 2 — The Journey:

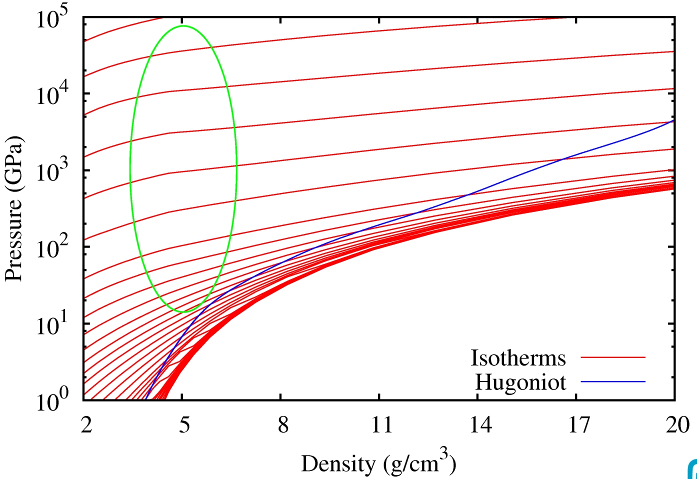
EOS model analysis and construction

Three Prior EOS models

- SESAME 5190 (LANL):
  - INFERNO electronic term
  - Uses CRIS fluid model
  - Solid phase with melt included
- LEOS 540 (LLNL):
  - QEOS based
  - TF electronic term
- XEOS 540 (LLNL):
  - Pergatorio electronic term
  - Solid/liquid phases with zero latent heat of melting

SESAME 5190 Hugoniot Softness

- Electronic term clearly at issue
- J.D. Johnson points out the problem: interpolation
- Saha to INFERNO interpolation from 4.6 – 40.0 g/cm^3
- “Bumps” in pressure isotherms result



EOS construction strategy

Standard Helmholtz free energy separation:

$$F(\rho, T) = F_c(\rho) + F_i(\rho, T) + F_e(\rho, T)$$

Construction details:

- solid and fluid models
- independent free energy terms for each model
- semi-empirical free energy forms
- calibrate parameters to wide range of data

Thermal electronic term

$$F_e(\sigma, T) = -c_e(\sigma, T)\,T \log\left(1 + \frac{B_e(T)T}{2c_e(\sigma,T)}\sigma^{-\gamma_e(\sigma,T)}\right)$$

where:

$$B_e(T) = \frac{2}{T^2}\int_0^T \int_0^{T'} \beta(\tau)\,d\tau\,dT'$$

$$\beta(T) = \beta_i + \left(\beta_0 - \beta_i + \beta_m \frac{T}{T_b}\right)\exp(-T/T_b)$$

$$c_e(\sigma, T) = \frac{3R}{2}\left(Z + \frac{\sigma_z T_z^2(1-Z)}{(\sigma+\sigma_z)(T^2+T_z^2)}\right)$$

$$\gamma_e(\sigma, T) = \gamma_i + (\gamma_0 - \gamma_i)\exp\left(-T/T_g\right)$$

- Simplified version of semi-empirical Bushman-Lomonosov-Fortov (BLF) form
- Satisfies build in limits of degenerate and ideal electron gases
- Nine adjustable parameters in fluid, seven in solid ($\sigma_z = 0$)

Thermal ionic terms

Solid (Debye model with cutoff):

$$F_i = \frac{R}{A}\left(\frac{9}{8}\theta + F_D\left(\theta/T\right) - F_D\left(\theta_n/T\right)\right)$$

where:

$$\theta = \theta_r \sigma^{2/3} \exp(\gamma_r - \gamma) \qquad \gamma = (\gamma_r - 2/3)/\sigma + \gamma_\infty$$

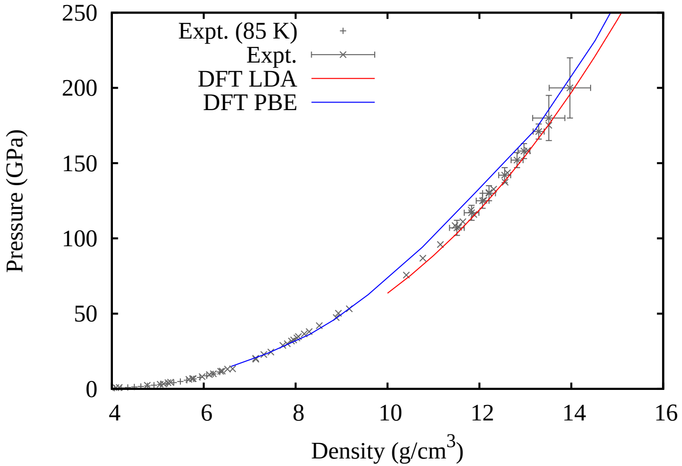
$$F_D(x) = 3T \log(1 - \exp(-x)) - TD(x)$$

$$\theta_n = 0.2 \frac{\theta^2 A M_0}{2\hbar^2}\left(\frac{3AM_0}{4\pi\rho}\right)^{2/3} \qquad D(x) = \frac{3}{x^3}\int_0^x \frac{t^3}{e^t - 1} dt$$

Liquid (CRIS model):

- Variational hard-sphere model
- Includes first order soft-sphere corrections
- Cold curve as input with two additional parameters

Isothermal compression data



- fcc-hcp transition completes at 70 GPa
- model single phase via an interpolating cold curve

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Series cold curve form: compression

$$F_c = \int_1^\sigma P_c(x) x^{-2} dx \qquad \sigma = \rho/\rho_{00}$$

- Vinet form successful but incorrect asymptote
- Use power series to match Vinet at equilibrium and Thomas-Fermi limit

$$P_c(Y) = \sum_{i=-2}^{5} b_i Y^i \qquad Y = \sigma^{1/3}$$

Constraint equation			Description
$\lim_{Y\to\infty} P_c(Y)$	=	$P_{TF} Y^5$	TF limit
$P_c(5)$	=	P_{TFK}	TF corrections limit ($P \sim Y^4$)
$P_c(1)$	=	0	Equilibrium pressure
$K_c(1) = \frac{Y}{3}\frac{dP_c}{dY}(1)$	=	K_0	Equilibrium bulk modulus
$\frac{dK_c}{dP}(1)$	=	K_0'	Pressure curvature
$K_c''(1)$	=	K_V''	Equilibrium Vinet match
$P_c(5/4)$	=	αP_{V1}	Vinet matching (adjustable)
$P_c(7/4)$	=	βP_{V2}	Vinet matching (adjustable)

- Three parameters to match equilibrium behavior
- Two parameters (α, β) to transition between fcc and hcp phases
- Linear solve of constraint equations for b_i

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Series cold curve form: expansion

- Compression form unreliable in expansion
- Series expansion form matches compression form pressure and first two derivatives at a crossover density ρ_{LJ} (determines f_1, f_2, f_3)
- Simple, generalized Lennard-Jones (LJ) form for solid (2 parameters)

$$F_c(\rho) = f_1 \rho^{f_2} - f_3 \rho^{f_{LJ}} + E_B$$

- Adjustable Van der Waals (VdW) based form for fluid (3 parameters)

$$F_c(x = \rho/\rho_{LJ}) = E_B + x \sum_{i=1}^{6} f_i x^i$$

- extra term in VdW form prevents unphysical oscillation

Model Calibration

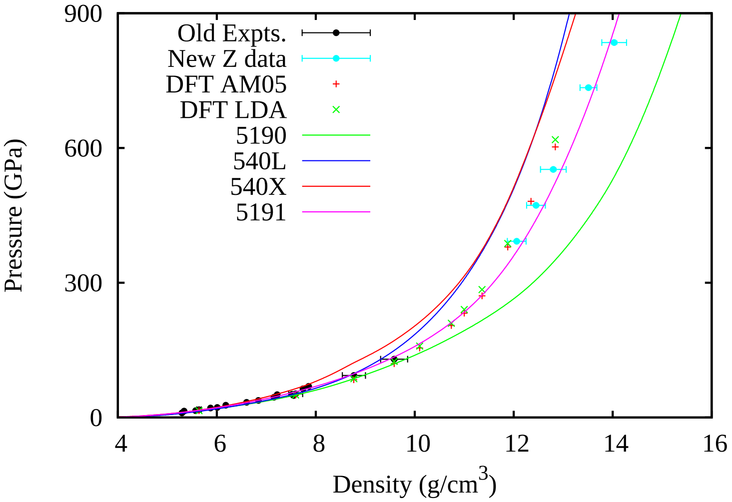
- Solid model:
  - 18 parameters
  - Custom series cold curve with LJ expansion form
  - Debye and BLF models
- Fluid model:
  - 19 parameters
  - Custom series cold curve with VdW expansion form
  - CRIS and BLF models
- Data:
  - Experimental, DFT isotherms
  - Experimental, DFT, QMC melting curves
  - Experimental, DFT Hugoniot
  - Experimental vapor dome and expansion isobars

Part 3 — The Results:

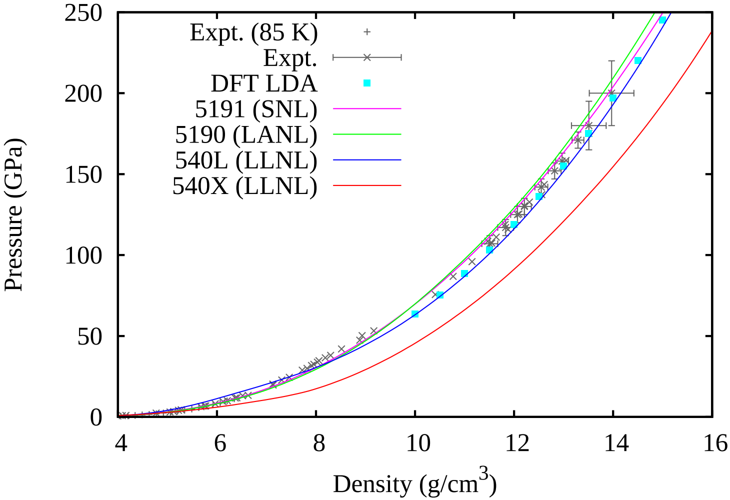
Comparing old and new EOS models with data

- All EOS model data obtained from tables
- Transfinite Coon's patch interpolation
- Rational interpolation on patch boundaries use central finite difference derivatives on the table grid

Liquid Hugoniot

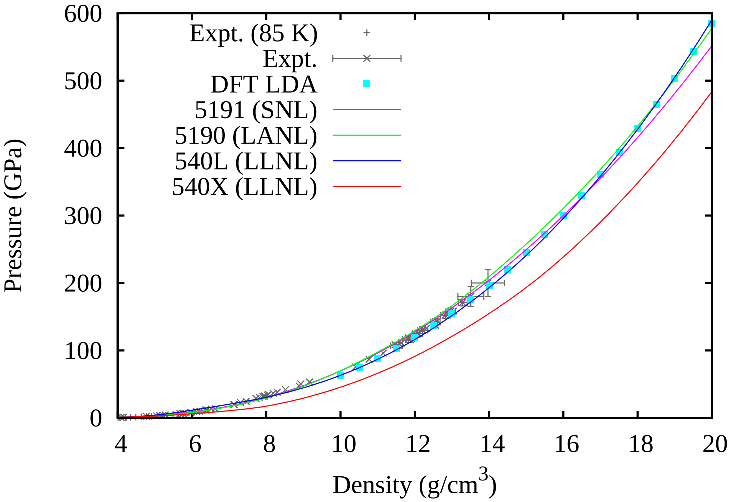


Isothermal compression curves



- 540X too soft, 540L stiff at low densities
- 5190 and 5191 interpolate between fcc and hcp phases

Isothermal compression curves: higher pressure



- 5190, 5191 soften at high density, interpolating to TF limit

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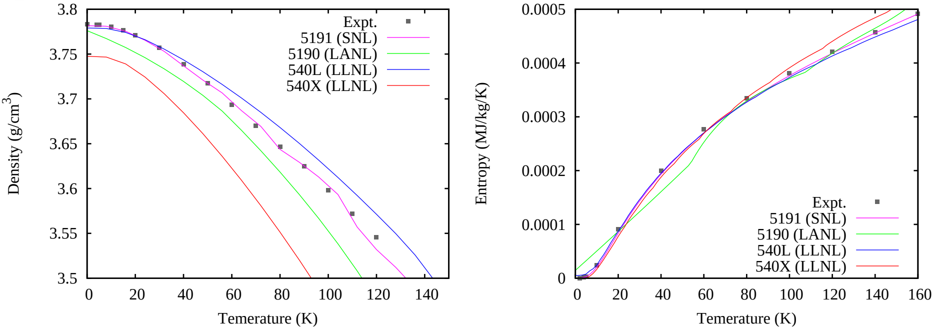
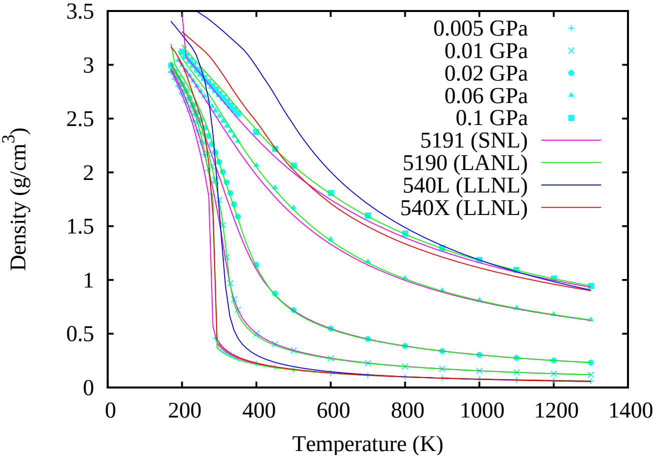
Ambient pressure curves



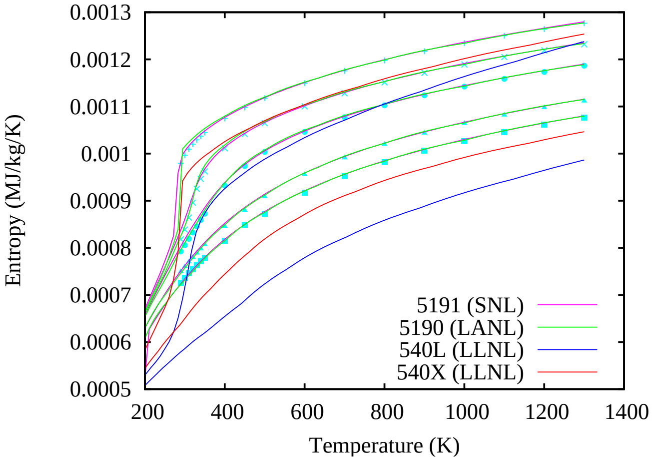
- 5191 follows Touloukian density data closely, waviness from interpolation artifacts
- 540L and 5191 follow Hultgren entropy data
- 5191 has strange entropy behavior at low temperatures
- 540X entropy too large at high T due to melt treatment

Fluid density isobars near critical point



- Points are from fits to experimental measurements (Vargaftik, Streett)
- Only highest and lowest pressures shown for 540L, 540X

Fluid entropy isobars near critical point

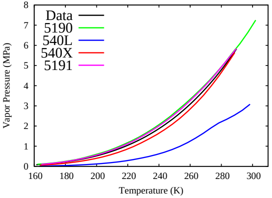


- 540L, 540X in poor agreement with data (Vargaftik)
- Due to melting treatment

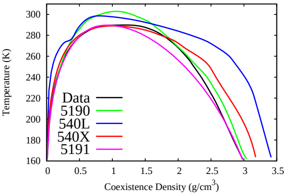
Critical point parameters

Model	T_c (K)	ρ_c (g/cm^3)	P_c (MPa)
Expt.	289.7	1.110	5.84
5191	289.6	0.943	5.84
5190	302.0	1.190	7.25
540X	288.6	1.134	5.64
540L	298.4	0.875	3.08

- 540L poor, 5190 has high pressure
- 540X slightly low pressure, but overall best
- 5191 density off due to approximations in CRIS model
- 5191 only table with liquid-vapor Maxwell constructions

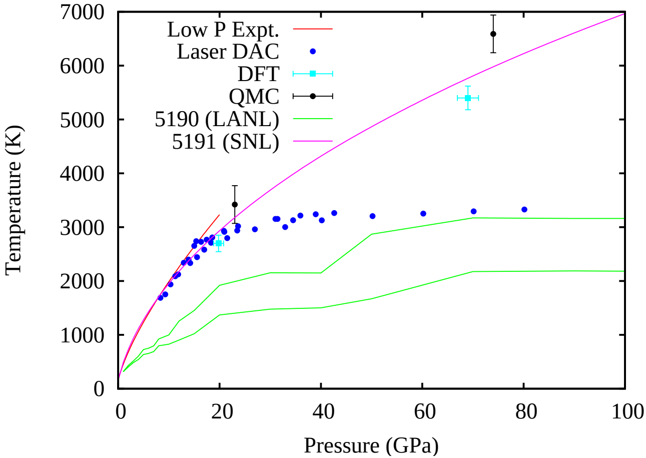


vapor pressure



vapor dome

Melting Curve



- 5190 and 5191 contain melt Maxwell constructions
- Low pressure data agrees with DAC to 20 GPa
- Fluid-fcc-hcp triple point expected around 20 GPa
- DFT and QMC calculations disagree with high pressure DAC

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5191 available from LANL SESAME database

Thanks to:

Thomas Mattsson, Rudy Magyar, Seth Root, David Hanson
Luke Shulenburger, J. D. Johnson, Phil Sterne, Jerry Kerley

Questions?

Parameters for 5191 version 2

Solid model parameters		Fluid model parameters	
ρ_{00}	3.8232 g/cm^3	ρ_{00}	3.7629 g/cm^3
K_0	3.7866 GPa	K_0	3.6590 GPa
K_0'	7.2903	K_0'	7.5703
ρ_{LJ}	3.7808 g/cm^3	ρ_{LJ}	3.7253 g/cm^3
f_{LJ}	2.5394	f_4	-0.26962 MJ/kg
α	0.95	f_5	0.010431 MJ/kg
β	0.69	f_6	0.013481 MJ/kg
E_B	0.12588 MJ/kg	E_B	0.12163 MJ/kg
θ_r	48.890 K	B_{exp}	2.1180 g$^{1/3}$/cm
γ_r	2.6285	E_s	0.004029 MJ/kg
ρ_r	3.5033 g/cm^3	ρ_r	5.2756 g/cm^3
T_b	5026.4 K	T_b	13101. K
T_g	300000. K	T_g	76808. K
		T_z	300000 K
σ_z	0.0	σ_z	2.7561
β_i	2.0299e-10 MJ/kg/K^2	β_i	1.1233e-08 MJ/kg/K^2
β_0	1.0e-12 MJ/kg/K^2	β_0	1.0006e-12 MJ/kg/K^2
β_m	4.0004e-11 MJ/kg/K^2	β_m	3.1663e-08 MJ/kg/K^2
γ_i	0.23503	γ_i	0.30193
γ_0	0.40218	γ_0	3.4922e-5

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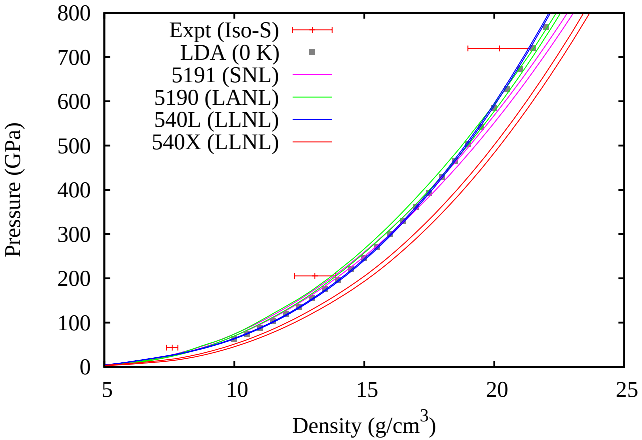
Liquid Isentrope



- 3 g/cm^3, 163 K isentrope with 298 K compression curves
- LDA fcc cold curve and LDA isentrope
- Experimental isentrope (Urlin)