Equation of State for PbLi

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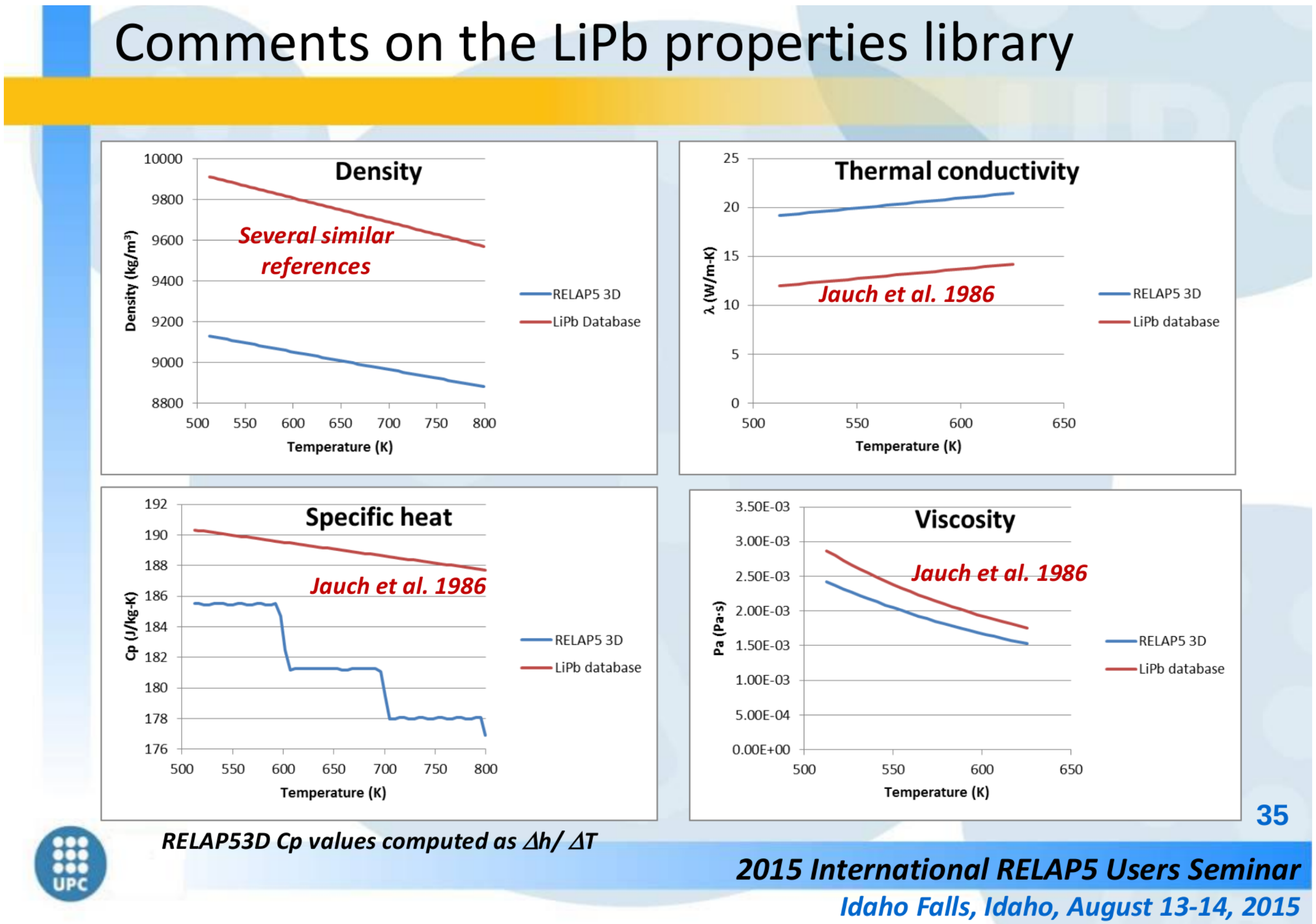
User Problem #15059

- PbLi properties differ by 10-15% from generally accepted measured values (L. Batet, 2015 IRUG):



Some History

- The capability to model alternate fluids was added to RELAP/ATHENA in the early 1990s
- Liquid metal thermodynamic property tables (P, v, T, c_p, α, κ_T) were computed using equations of state published for pure fluids in the 1970s[1]
- These were fitted to data inexactly owing to limitations in computing power at the time
- The RELAP5-3D implementation for mixtures uses a mass-weighted average of the pure component parameters
- Inaccuracies arise because:
  - Parameters are exponents or are raised to exponents
  - PbLi mixtures form "some of the most dramatically non-ideal solutions known"[2]

[1] D. A. Young, A soft-sphere model for liquid metals, UCRL-52352, LLNL (1977).

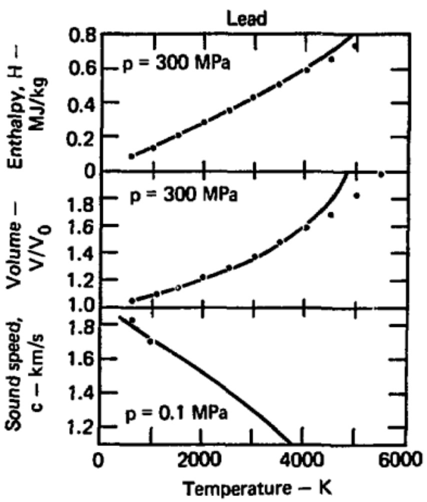
[2] R. E. Buxbaum, *Journal of the Less-Common Metals* **97** (1984) 27-38.

Soft Sphere equation of state

- Helmholtz free energy $a(v,T)$:

$$\frac{a}{NkT} = -1-\ln\left(\frac{v\,(2\pi kT)^{\frac{3}{2}}}{h^3 N^{\frac{5}{2}}}\right)+C_n\left(\frac{\sigma^3}{\sqrt{2}}\frac{N}{v}\right)^{\frac{n}{3}}\left(\frac{\varepsilon}{kT}\right)+\frac{1}{2}(n+4)\,Q\left(\frac{\sigma^3}{\sqrt{2}}\frac{N}{v}\right)^{\frac{n}{9}}\left(\frac{\varepsilon}{kT}\right)^{\frac{1}{3}}-\left(\frac{\sigma^3}{\sqrt{2}}\frac{N}{v}\right)^{m}\left(\frac{\varepsilon}{kT}\right)+\frac{E_{coh}}{NkT}$$

- Fit parameters: n, m, Q, ε, $\sigma^3/\sqrt{2}$
- Original fitting procedure[1]:
  - Fix n, m, and Q
  - Solve P=0 and u=h_m at (v_m, T_m) for ε, $\sigma^3/\sqrt{2}$
  - Adjust n, m, and Q to better match data
  - Not "carried… to an extreme precision of fit"[1]



PbLi parameters

N	$3.4772 \times 10^{24}\ atom/kg$
C_n	6.0718
E_{coh}	$1.096 \times 10^{6}\ J/kg$
n	10.951
m	1.048
Q	0.853
ε	$1.74885 \times 10^{-18}\ J/atom$
$\sigma_{ss}^3/\sqrt{2}$	$9.19694 \times 10^{-30}\ m^3/atom$

- New strategy:
  - Actually fit the EOS to all available thermodynamic property data for PbLi

[1] D. A. Young, A soft-sphere model for liquid metals, UCRL-52352, LLNL (1977).

Available Data

Density: S. V. Stankus et al., *High Temperature* **44** n. 6 (2006) 829-837.

Vapor Pressure (pure Pb): A. N. Nesmeyanov, “Vapor Pressure of the Chemical Elements,” Elsevier, Amsterdam, 1963.

Vapor pressure should be almost identical to pure Pb because of low activity of Li in Pb

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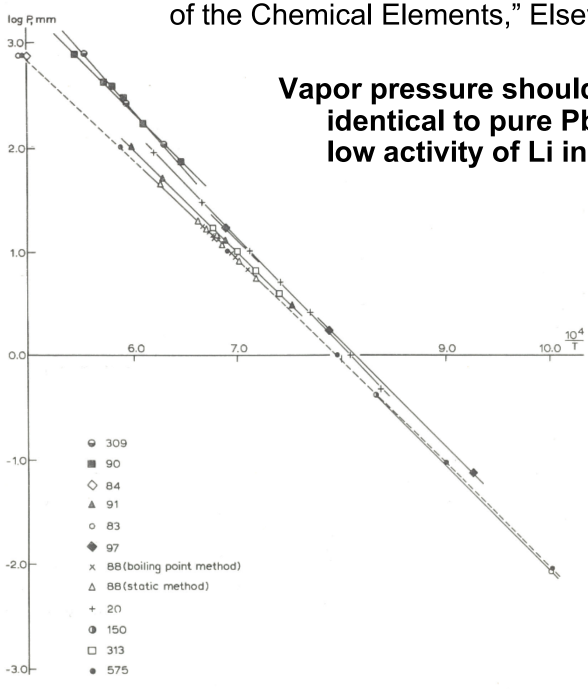


Fig. 114. Experimental data on the vapor pressure of lead.

figure given in [309], and the latter should be considered too high (see page 29).

In [83, 84], the boiling point of lead was determined at 760 mm Hg in an inert atmosphere. The value was obtained from the horizontal segment of the heating curve plotted from readings of a thermocouple immersed in the metal. In the first mentioned study, the value obtained for the boiling

Specific Heat: U. Jauch et al., KfK report 4144, 1986.

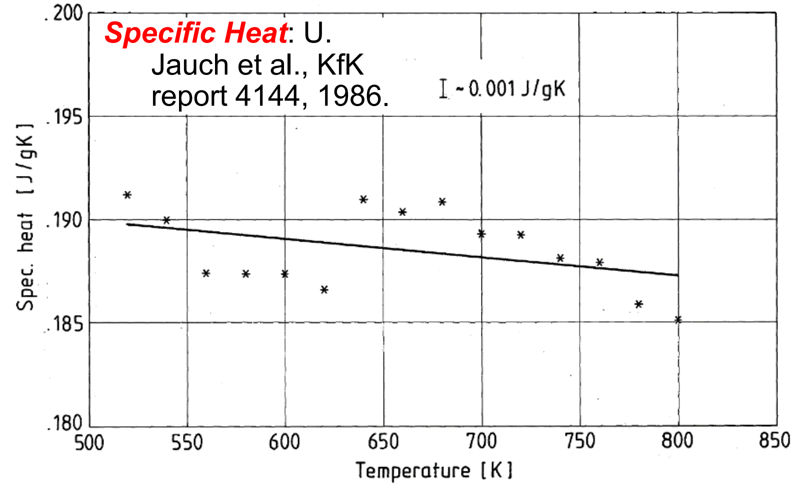


Fig. 1b: Specific heat at constant pressure of liquid Li(17)Pb(83).

Sound Speed: Y. Ueki et al., *Fusion Science and Technology* **56** (2009) 846-850.

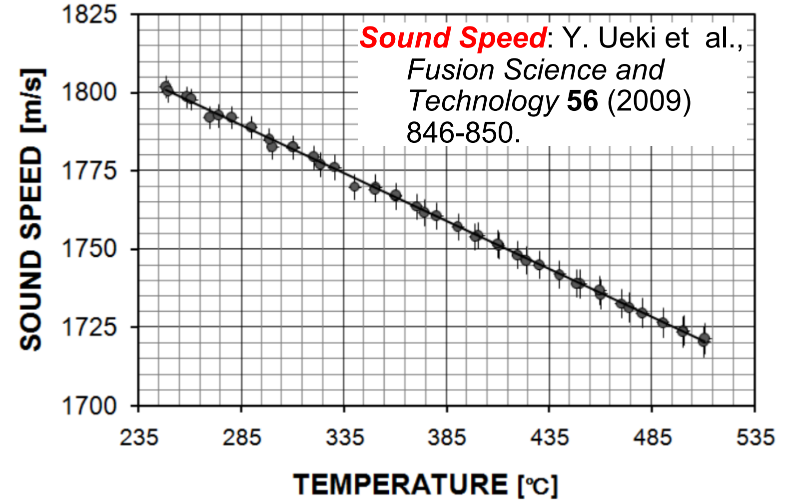


Fig. 7 Temperature dependency of sound speed in liquid Pb-17Li

Computing properties from the EOS

- All thermodynamic properties are derivable from the Helmholtz free energy:

$$P(v,T) = -\left(\frac{\partial a}{\partial v}\right)_T$$

$$s(v,T) = -\left(\frac{\partial a}{\partial T}\right)_v$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_P = T\left[\left(\frac{\partial s}{\partial T}\right)_v - \left(\left(\frac{\partial P}{\partial T}\right)_v^2 \Big/ \left(\frac{\partial P}{\partial v}\right)_T\right)\right]$$

$$w = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s} = v\sqrt{\left(\left(\frac{\partial P}{\partial T}\right)_v^2 \Big/ \left(\frac{\partial s}{\partial T}\right)_v\right) - \left(\frac{\partial P}{\partial v}\right)_T}$$

Fitting Procedure

- Simultaneously minimize the (square) of the difference between all measured and calculated values:

$$\zeta^2 = \sum_{1=m}^{M} W_m \left(\frac{y_{EOS,m} - y_{data,m}}{y_{data,m}} \right)^2$$

- Minimization performed using the nlm package in R[1]
- Evaluating y_{EOS} not trivial:
  - Comparing to $\rho(T)$ data requires finding roots of $P(\rho,T)=P_{atm}$
  - Need to find all three and select the one corresponding to liquid
  - Same root finding necessary to evaluate $c_p(\rho,T)$ and $w(\rho,T)$
  - May not converge or find all roots when parameters are changing during optimization
  - Particularly for the saturation pressure, which requires solving a system of equations...

[1] *R: A Language and Environment for Statistical Computing*, R Foundation for Statistical Computing, Vienna, Austria, http://www.R-project.org (2016).

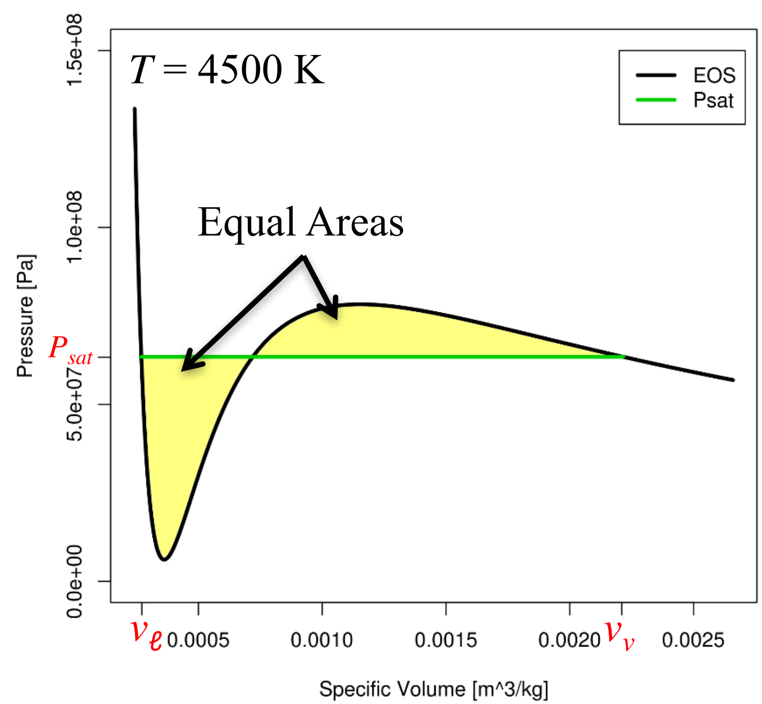
Vapor Pressure

- Previously, the saturated volumes were computed by setting $P_{EOS}(v, T_{sat})$ equal to an *empirical* $P_{sat}(T_{sat})$ and solving for v
- But, the EOS *predicts* a unique $P_{sat}(T)$: instead, we can compare this to data, i.e. use vapor pressure data in the fit
- Computed from the EOS based on the fact that phases are in thermal, mechanical, and chemical equilibrium, i.e. they have the same:
  - Temperature (T_{sat})
  - Pressure (P_{sat})
  - Gibbs free energy:

$$P_{sat} = P\left(v_\ell, T_{sat}\right)$$

$$P_{sat} = P\left(v_v, T_{sat}\right)$$

$$P_{sat}\left(v_\ell - v_v\right) = a\left(v_v, T_{sat}\right) - a\left(v_\ell, T_{sat}\right)$$



Generalizing the EOS

- The form of the soft sphere equation of state proved not flexible enough to match density, specific heat, sound speed, and vapor pressure data simultaneously
- Reorganize:

$$d_1 = \frac{n}{3} \quad d_2 = \frac{n}{9} \quad d_3 = m \quad s_0 = -1 - \ln\left[\frac{(2\pi k T_m)^{\frac{3}{2}}}{h^3 \rho_m N^{\frac{5}{2}}}\right] \quad u_0 = \frac{E_{coh}}{R_s T_m} \quad n_1 = \left(N\rho_m \frac{\sigma_{ss}^3}{\sqrt{2}}\right)^{\frac{n}{3}} \left(\frac{\varepsilon}{kT_m}\right) C_n$$

$$t_1 = 1 \quad t_2 = \frac{1}{3} \quad t_3 = 1 \quad n_2 = \frac{1}{2}(n+4)\, Q \left(N\rho_m \frac{\sigma_{ss}^3}{\sqrt{2}}\right)^{\frac{n}{9}} \left(\frac{\varepsilon}{kT_m}\right)^{\frac{1}{3}} \quad n_3 = -\left(N\rho_m \frac{\sigma_{ss}^3}{\sqrt{2}}\right)^{m} \left(\frac{\varepsilon}{kT_m}\right)$$

$$\frac{a}{R_s T} = s_0 + u_0 \left(\frac{T_m}{T}\right) + ln\left(\frac{\rho}{\rho_m}\left(\frac{T_m}{T}\right)^{\frac{3}{2}}\right) + \sum_{i=1}^{3} n_i \left(\frac{T_m}{T}\right)^{t_i} \left(\frac{\rho}{\rho_m}\right)^{d_i}$$

- This is special case of a widely used standard form[1]:

$$a = a^o + a^r$$

$$\frac{a^o(\rho, T)}{R_s T} = c^{II} + c^{I}\left(\frac{T_r}{T}\right) + \ln\left(\frac{\rho}{\rho_r}\left(\frac{T_r}{T}\right)^{c_0}\right) + \sum_{i=1}^{I_{Pol}} c_i \left(\frac{T_r}{T}\right)^{t_i}$$

$$\frac{a^r(\rho, T)}{R_s T} = \sum_{i=1}^{I_{Pol}} n_i \left(\frac{T_r}{T}\right)^{t_i} \left(\frac{\rho}{\rho_r}\right)^{d_i} + \sum_{i=1+I_{Pol}}^{I_{Pol}+I_{Exp}} n_i \left(\frac{T_r}{T}\right)^{t_i} \left(\frac{\rho}{\rho_r}\right)^{d_i} \exp\left(-\gamma_i \left(\frac{\rho}{\rho_r}\right)^{p_i}\right)$$

[1] R. Span, “Multiparameter Equations of State,” Springer, Berlin, 2000.

Fitting the Generalized EOS

$$a = a^o + a^r$$

$$\frac{a^o(\rho,T)}{R_sT} = c^{II} + c^I\left(\frac{T_r}{T}\right) + \ln\left(\frac{\rho}{\rho_r}\left(\frac{T_r}{T}\right)^{c_0}\right) + \sum_{i=1}^{I_{Pol}} c_i\left(\frac{T_r}{T}\right)^{t_i}$$

$$\frac{a^r(\rho,T)}{R_sT} = \sum_{i=1}^{I_{Pol}} n_i\left(\frac{T_r}{T}\right)^{t_i}\left(\frac{\rho}{\rho_r}\right)^{d_i} + \sum_{i=1+I_{Pol}}^{I_{Pol}+I_{Exp}} n_i\left(\frac{T_r}{T}\right)^{t_i}\left(\frac{\rho}{\rho_r}\right)^{d_i}\exp\left(-\gamma_i\left(\frac{\rho}{\rho_r}\right)^{p_i}\right)$$

- Start with the best soft sphere fit
- Round density exponents to nearest integer
- Fit leading coefficients and temperature exponents
- Add a single exponential term
  - Systematically try different combinations of the exponents d_i and p_i
  - Examine impact on fit
  - Keep the term that improves the fit most significantly
  - Resume simultaneous fitting, including the new term
- Add one polynomial term to the Helmholtz free energy of the ideal gas
  - To fix minor imperfections in specific heat and sound speed fits

Final Result

$$\frac{a}{R_s T} = s_0 + u_0\left(\frac{T_m}{T}\right) + ln\left(\frac{\rho}{\rho_m}\left(\frac{T_m}{T}\right)^{\frac{3}{2}}\right) + \sum_{i=1}^{5} n_i \left(\frac{T_m}{T}\right)^{t_i}\left(\frac{\rho}{\rho_m}\right)^{d_i} exp\left(-\gamma_i\left(\frac{\rho}{\rho_m}\right)^{p_i}\right)$$

i	n_i	t_i	d_i	γ_i	p_i
1	-12.30	0.8739	0	0	0
2	-75.40	1.008	1	0	0
3	18.29	0.9647	3	0	0
4	1.849	1.369	4	0	0
5	33.02	0.4736	2	1	1

$T_m = 508.1$ K

$\rho_m = 9915.5\ \mathrm{kg/m^3}$

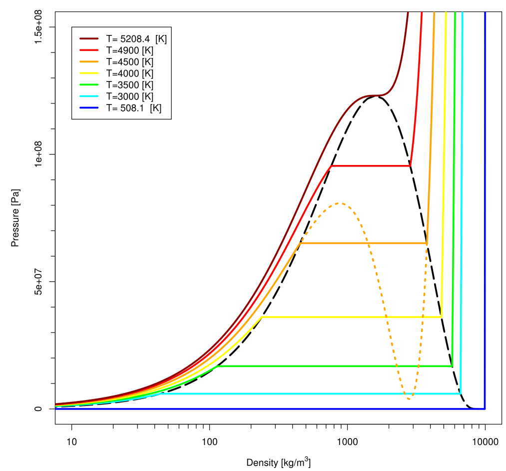
$u_0 = 59.37$

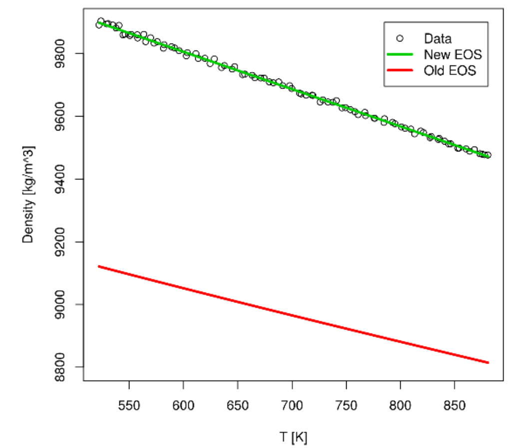
$s_0 = -3.94$

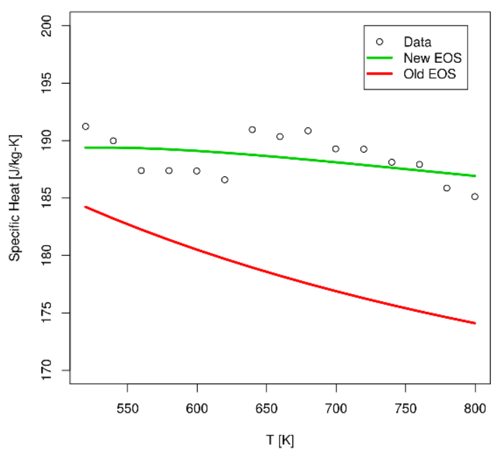
$T_c = 5208.4\,\mathrm{K}$

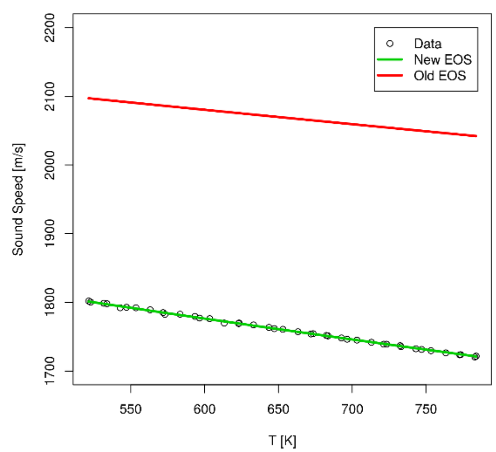
$P_c = 123.05\,\mathrm{MPa}$

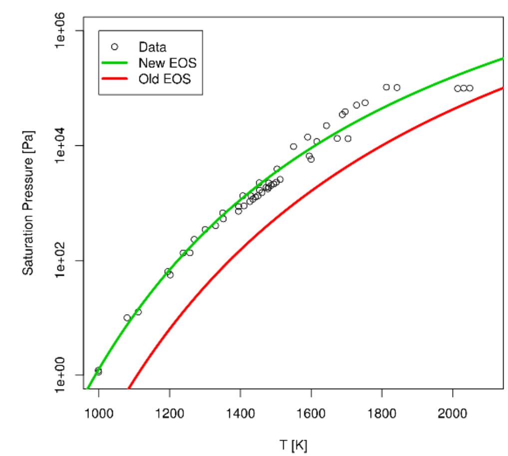
$\rho_c = 1593.0\,\frac{\mathrm{kg}}{\mathrm{m^3}}$











Status of RELAP5-3D implementation

- New equation of state and transport properties for PbLi have been implemented in RELAP5-3D
- Final verification testing to be performed
- Will be included in new RELAP5-3D version
- Result published:
  - P. W. Humrickhouse and B. J. Merrill, “An equation of state for liquid $Pb_{83}Li_{17}$,” Fusion Engineering and Design **127** (2018) 10-16.

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