Equation of State for PbLi

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

Comments on the LiPb properties library

RELAP53D Cp values computed as $\Delta h/\Delta T$
Some History

- The capability to model alternate fluids was added to RELAP/ATHENA in the early 1990s.
- Liquid metal thermodynamic property tables \((P, v, T, c_p, \alpha, \kappa_T)\) were computed using equations of state published for pure fluids in the 1970s\(^1\)
- These were fitted to data inexactaly 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”\(^2\).

Soft Sphere equation of state

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

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

- Fit parameters: $n$, $m$, $Q$, $\varepsilon$, $\sigma^3/\sqrt{2}$
- Original fitting procedure\(^1\):
  - Fix $n$, $m$, and $Q$
  - Solve $P=0$ and $u=h_m$ at $(v_m, T_m)$ for $\varepsilon$, $\sigma^3/\sqrt{2}$
  - Adjust $n$, $m$, and $Q$ to better match data
  - Not “carried… to an extreme precision of fit”\(^1\)
- New strategy:
  - Actually fit the EOS to all available thermodynamic property data for PbLi

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\(^1\) D. A. Young, A soft-sphere model for liquid metals, UCRL-52352, LLNL (1977).
Available Data


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


\[ \text{Specific heat} \left[ \text{J/gK} \right] = -0.001 \]  


![Sound Speed Graph](image)

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

![Vapor Pressure Graph](image)

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

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 point is 1765 °C.
Computing properties from the EOS

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

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

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

\[ c_p = T \left( \frac{\partial s}{\partial T} \right)_p = T \left[ \left( \frac{\partial s}{\partial T} \right)_v - \left( \frac{\partial P}{\partial T} \right)_v / \left( \frac{\partial P}{\partial v} \right)_T \right] \]

\[ w = \sqrt{\left( \frac{\partial P}{\partial \rho} \right)_s} = v \sqrt{\left( \frac{\partial P}{\partial T} \right)_v / \left( \frac{\partial s}{\partial T} \right)_v - \left( \frac{\partial P}{\partial v} \right)_T} \]
Fitting Procedure

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

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

• 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...

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:

\[
P_{sat} = P(v_{\ell}, T_{sat})
\]
\[
P_{sat} = P(v_{v}, T_{sat})
\]
\[
P_{sat}(v_{\ell} - v_{v}) = a(v_{v}, T_{sat}) - a(v_{\ell}, T_{sat})
\]

$T = 4500$ K

Equal Areas
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:

\[ d_1 = \frac{n}{3} \quad d_2 = \frac{n}{9} \quad d_3 = m \quad s_0 = -1 - \ln \left( \frac{(2\pi k T_m)^{3/2}}{h^3 \rho_m N^{3/2}} \right) \]

\[ u_0 = \frac{E_{coh}}{R_s T_m} \quad n_1 = \left( N \rho_m \frac{\sigma_{ss}^3}{\sqrt{2}} \right)^{3/2} \left( \frac{\varepsilon}{k T_m} \right) C_n \]

\[ t_1 = 1 \quad t_2 = \frac{1}{3} \quad t_3 = 1 \quad n_2 = \frac{1}{2} (n + 4) Q \left( N \rho_m \frac{\sigma_{ss}^3}{\sqrt{2}} \right)^{3/2} \left( \frac{\varepsilon}{k T_m} \right)^{3/2} \quad n_3 = - \left( N \rho_m \frac{\sigma_{ss}^3}{\sqrt{2}} \right)^{m} \left( \frac{\varepsilon}{k T_m} \right) \]

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

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

\[ a = a^o + a^r \]

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

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

Fitting the Generalized EOS

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

\[ \frac{a^r (\rho, T)}{R_s T} = \sum_{i=1}^{IPol} n_i \left( \frac{T_r}{T} \right)^{t_i} \left( \frac{\rho}{\rho_r} \right)^{d_i} + \sum_{i=1}^{IPol+IExp} n_i \left( \frac{T_r}{T} \right)^{t_i} \left( \frac{\rho}{\rho_r} \right)^{d_i} \exp \left( -\gamma_i \left( \frac{\rho}{\rho_r} \right)^{p_i} \right) \]

- 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

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

| \( i \) | \( n_i \) | \( t_i \) | \( d_i \) | \( \gamma_i \) | \( p_i \) |
|---|---|---|---|---|
| 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 |

\( T_m = 508.1 \text{ K} \)
\( \rho_m = 9915.5 \text{ kg/m}^3 \)
\( T_c = 5208.4 \text{ K} \)
\( P_c = 123.05 \text{ MPa} \)
\( u_0 = 59.37 \)
\( s_0 = -3.94 \)
\( \rho_c = 1593.0 \text{ kg/m}^3 \)
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:
Future Directions in FSE Research

- Strategy based on FES guidance and 2013 FES Peer Review Comments

- Materials Research: Fusion materials, including tungsten irradiated, will be studied at high temperature and heat flux to measure tritium retention and permeation. Dust explosion measurements for fusion materials will continue in support of licensing and computer code development activities.

- Code Development: for the near term, a newer version of MELCOR for ITER will to be completed that includes tritium transport and dust explosion models. Long-term: Multi-dimensional safety code capabilities needs to be developed that take advantage of parallel computing (example RELAP 7).

- Risk and Licensing: FSP's evolving failure rate database will be expanded to include maintenance data from existing tokamaks. Risk-informed safety analysis methods (example RISMC Toolkit) will be studied for application to an FNSF. Continue ASME codes and standards and licensing framework development.

- Collaborations: Participation in existing collaborations to leverage other institution's capabilities and reduce duplication of effort. STAR will move towards being more effective FES User Facility.

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