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Thermophysical properties and thermodynamic equation of state of lithium-lead for nuclear fusion reactor safety calculations

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Abstract

One of the most promising designs for the breeding blanket is the water cooled lithium lead, extensive efforts have been carried out over the years to study the interaction between water and lithium-lead in case of a loss of coolant accident, both experimentally and numerically. This possible accident scenario requires a numerical tool able to simulate the complex phenomena involved. The SIMMER code is currently the best candidate since it is used to perform safety analysis for liquid metal nuclear fission reactors. Even though, different milestones have been reached for the adaptation of SIMMER code for the Lithium-Lead/water interaction, a comprehensive work on the lithium-lead equation of state (EOS) and thermo-physical properties has never been carried out. The investigation of the EOS and thermo-physical properties of SIMMER is conducted and the most updated data on lithium-lead is collected. Using the experimental data, the new SIMMER analytical equations for lithium-lead are obtained. The implementation of EOS and thermo-physical properties of lithium-lead in SIMMER enables the real fluid behavior of the liquid metal and they will represent more realistically the conditions occurring during an interaction between lithium-lead and water during nuclear fusion reactor accidents.

Keywords: lithium-lead, equation of state, SIMMER, WCLL

(Some figures may appear in colour only in the online journal)

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1. Introduction

The water cooled lithium lead breeding blanket is among the most promising designs for the breeding blanket component. This breeding blanket uses subcooled liquid water at PWR conditions as coolant and the liquid metal lithium-lead as tritium breeder [1]. Among all the possible compositions of lithium lead alloy the most studied is the one near the eutectic point, namely with atomic percentage of lithium 17 at.%. This is due to the low lithium chemical activity, compared to other alloys composition, yet an acceptable breeding ratio for tritium generation [2, 3].

The critical concern for this specific breeding blanket design is the not negligible eventuality of a loss of coolant accident, which can occur inside the breeding blanket after a rupture of a water cooling tube. The interaction is characterized by an extremely rapid thermodynamic transient caused by the difference in pressure and temperature between the two fluids but also characterized by a chemical interaction between water and lithium contained in the liquid metal. The complexity of the reaction and the necessity of having a numerical tool able to perform safety calculations led to the use of the SIMMER code family. The SIMMER code is a multiphase, multicomponent, three-velocity field fluid-dynamics Eulerian code developed for the safety analysis of liquid metal fast reactors, by the Japan Atomic Energy Agency (JAEA) [4]. A lot of extensive work has been carried out to adapt the SIMMER code to the nuclear fusion framework but a comprehensive and complete work on the thermophysical properties and the thermodynamic equation of state (EOS) used inside SIMMER have never been carried out [5].

Water is used in some designs of liquid metal fast reactors, which is a material originally modeled in SIMMER code. It can be used as coolant and the thermophysical properties and EOS are already developed. However, the lithium-lead is a liquid metal alloy thought specifically for the nuclear fusion reactor breeding blankets, which has never been developed for the SIMMER code. Since it is necessary to have both liquid fluids inside the same computational cell lithium-lead is developed as fuel material. Indeed, the SIMMER code was developed considering the possibility to have liquid fuel in the event of a severe accident.

In this work, the lithium-lead thermophysical properties and EOS are developed for the SIMMER code and implemented replacing the liquid fuel material, with the most updated experimental data available in literature. The new SIMMER analytical equations for lithium-lead enable the real fluid behavior of the liquid metal and could potentially improve the safety calculations for nuclear fusion reactors using the WCLL BB as design.

This paper is subdivided as follows: in section 2, the EOS is analyzed, and the required analytical equations are developed. In section 3, the thermophysical properties are developed. In section 4, a summary of the SIMMER variables required for the implementation of the new EOS and thermo-physical properties is reported. Finally, in section 5 the conclusions are drawn.

2. Lithium lithium-lead EOS

2.1. SIMMER EOS description

The EOS plays a critical role in defining the relationships among thermodynamic variables such as pressure, temperature, and density, which are needed to close the full set of fluid-dynamic equations.

In numerical codes, there are two different approaches for implementing the EOS:

- Tabular EOS, where the thermodynamic state relationships needed by the code are represented in an external table which the code reads.
- Analytical EOS, which are analytical functions that represent the thermodynamic relationship between the state variables.

In previous versions of the SIMMER code family, both approaches were implemented but both had different issues. The use of a tabular EOS in the code presented several notable challenges. One of the primary drawbacks was the time-consuming process of searching and interpolating data from tables, which proved inefficient for complex multi-phase, multi-component flow simulations. Additionally, the need for iterative steps to achieve mechanical equilibrium further slowed down the computations. The earlier version of the analytical EOS faced significant issues, particularly in handling high-pressure conditions. Its simplified formulation led to inconsistencies, especially in determining vapor temperatures at elevated pressures. This resulted in numerous numerical problems, such as inaccuracies and instabilities in the simulations [6].

The standard version of the analytical EOS typically requires multiple fitting constants, which can be challenging to obtain, along with extensive data for the fitting process. To address this problem, a different analytical equation, known as Fitting-Free EOS (FFEOS), has been developed over the years by the SIMMER code developers. This approach significantly reduces the need for fitting constants and data, making it more suitable for implementing the lithium-lead EOS in SIMMER. While the FFEOS does result in a slight reduction in the code's numerical efficiency, this decrease is generally not significant for most cases of interest.

The key distinction between the standard analytical EOS in SIMMER and the FFEOS lies in the required fitting constants. The standard EOS requires fitting constants for all internal energies across different phases, but for Lithium-Lead, the necessary data for these constants are not available. The FFEOS, on the other hand, demands fewer parameters, making it more suitable for cases like lithium-lead where data are limited. However, the FFEOS starts from the vapor pressure curve and the vapor phase EOS to obtain also the internal energy of the liquid phase using the Clausius–Clapeyron equation. Therefore, the vapor phase region that is not extremely important for the phenomena occurring during lithium-lead/water interaction needs to be correctly represented for obtaining a coherent in the liquid phase zone.

The FFEOS requires the following constants:

- Critical parameters: $T_{\mathrm{cr}},\ v_{\mathrm{cr}},$ and p_{cr} are the thermodynamic variables values at the critical point, which are essential for constructing the vapor pressure curve and evaluating thermodynamic states in the gas phase.
- Temperature and density at the liquidus temperature: T_{LIQ} and v_{LIQ} are the values of the liquidus temperature and specific volume at the liquidus temperature. They are then used for the determination of the liquid density dependence on temperature.
- Pressure vapor curve fitting constants: $b_{\mathrm{L1}},\ b_{\mathrm{L2}}, b_{\mathrm{L3}}$ and b_{L4} are the fitting constants used for the vapor pressure curve. The vapor pressure curve is necessary for accurately representing the vapor phase and modeling the pressure effect on liquid density.
- Specific heat at a constant volume of infinitely diluted vapor at the liquidus temperature: $c_{\mathrm{vg,m}}$. It is used by the code to calculate vapor and liquid energy based on thermodynamic relationships.
- Saturated liquid specific volume fitting constant: $b_{\mathrm{SAT1}},\ b_{\mathrm{SAT2}}$ and b_{SAT3}. They are the fitting constants for the temperature dependence of the specific volume.
- 'Boundary Temperature': T_{BND} is used to model the liquid density near the critical point. For temperatures above this value, a different density–temperature analytical function is applied, which is better suited for modeling the liquid phase near the critical point.
- Adiabatic compressibility and fitting constant: $\beta_{\mathrm{s,LIQ,m}}$ and b, used to model the pressure dependence of density.

The temperatures of lithium-lead in the breeding blanket are anticipated to stay well below its boiling point in all potential scenarios. However, the SIMMER code still requires thermodynamic data for the vapor phase. Moreover, extending the thermophysical properties of lithium-lead over a broader temperature range is essential. As a result, obtaining the data needed for the fitting constants can be difficult.

2.2. Lithium-lead vapor EOS

The first parameters that are also used by the FFEOS are the critical parameters of lithium-lead. They are retrieved from literature, and they are [7]:

- Critical temperature: $T_{\mathrm{cr}}, = 5208\ [K]$
- Critical pressure: $p_{\mathrm{cr}} = 123.05\,[\mathrm{MPa}]$
- Critical specific volume: $v_{\mathrm{cr}} = 6.2775e-04\ \left[\mathrm{m}^3\,\mathrm{kg}^{-1}\right]$.

From these values it is possible to calculate the compressibility factor which is reported in equation (1)

$$Z_{\mathrm{c}} = \frac{p_{\mathrm{cr}}v_{\mathrm{cr}}}{R_{\mathrm{g}}T_{\mathrm{cr}}} \cong 0.3086. \tag{1}$$

The compressibility factor at the critical point is used for evaluating the validity of the critical parameters and it is similar to the lead compressibility factor and falls in the range expected for metals [8, 9].

Once the critical parameters have been determined it is possible to use experimental data on the vapor pressure, to obtain the fitting constants required for the vapor pressure curve. The SIMMER equation for the vapor pressure curve is reported in equation (2), it is defined as a function of the liquid temperature, T^+_{Lm}. The vapor pressure is p^+_{Lm} and $T_{\mathrm{Crt,M}}$ is the critical temperature,

$$p^+_{\mathrm{Lm}} = \exp\left[b_{\mathrm{L1,M}} + b_{\mathrm{L2,M}}T^+_{\mathrm{Lm}} + \frac{b_{\mathrm{L3,M}}}{T^+_{\mathrm{Lm}}} + b_{\mathrm{L4,M}}\ln\left(\frac{T^+_{\mathrm{Lm}}}{T_{\mathrm{Crt,M}}}\right)\right]. \tag{2}$$

The fitting constants $b_{\mathrm{L1,M}},\ b_{\mathrm{L2,M}},\ b_{\mathrm{L3,M}}$ and $b_{\mathrm{L4,M}}$ for the vapor pressure curve shown in equation (2) are obtained through a fitting process of the lithium-lead vapor pressure experimental data. The vapor pressure curve of lithium-lead has never been experimentally measured. Therefore, an alternative approach must be used. The methodology for obtaining this data involves using experimental data from the individual components of the liquid metal. Considering equation (3), the activity and mass fraction of each element can be used to derive the vapor pressure of the alloy starting from the vapor pressure of the single elements. This approach has been applied in various cases, such as with lead-bismuth [10] alloys and lithium-lead [7],

$$p_{\mathrm{sat,PbLi}} = x_{\mathrm{Li}}\gamma_{\mathrm{Li}}p_{\mathrm{sat,Li}} + x_{\mathrm{Pb}}\gamma_{\mathrm{Pb}}p_{\mathrm{sat,Pb}} \tag{3}$$

where $p_{\mathrm{sat},i}$ are the saturation pressure of lithium and lead, x_i are the mass fraction of both elements and γ_i are the activities. The vapor pressure of the single elements is obtained from literature [11, 12]. The mass fraction of the lithium-lead alloy can be derived from its atomic percentage. For the breeding blanket design, lithium constitutes 15.7% and lead 84.3% of the atomic composition. The activities, which depend on the temperature and Lead mass fraction, are determined using Gibbs free energy. The expression of the activity is reported in equation (4) and the Gibbs energy of lithium and lead, as a function of temperature and lead mass fraction are reported in equations (5) and (6) [13],

$$\gamma_i = \exp\left(\frac{G_i}{RT}\right) \tag{4}$$

$$\begin{aligned}G_{\mathrm{Li}} = {} & (-1388 + 0.0422T)x^2_{\mathrm{Pb}} + (7164 - 0.0416T)x^3_{\mathrm{Pb}} \\ & + (-17357 - 0.003T)x^4_{\mathrm{Pb}} + 22011x^5_{\mathrm{Pb}} - 14014x^6_{\mathrm{Pb}} \\ & + 3524x^7_{\mathrm{Pb}}\end{aligned} \tag{5}$$

$$\begin{aligned}G_{\mathrm{pb}} = {} & (-305 + 0.0224T) + (2776 - 0.0844T)x_{\mathrm{Pb}} \\ & + (-12134 + 0.1046T)x^2_{\mathrm{Pb}}(30307 - 0.0456T)x^3_{\mathrm{Pb}} \\ & + (-44871 + 0.003T)x^4_{\mathrm{Pb}} \\ & + 38828x^5_{\mathrm{Pb}} - 18125x^6_{\mathrm{Pb}} + 3524x^7_{\mathrm{Pb}}.\end{aligned} \tag{6}$$

Combining the equations above, it is possible to obtain the data necessary for the fitting of the vapor pressure curve which is shown in figure 1.

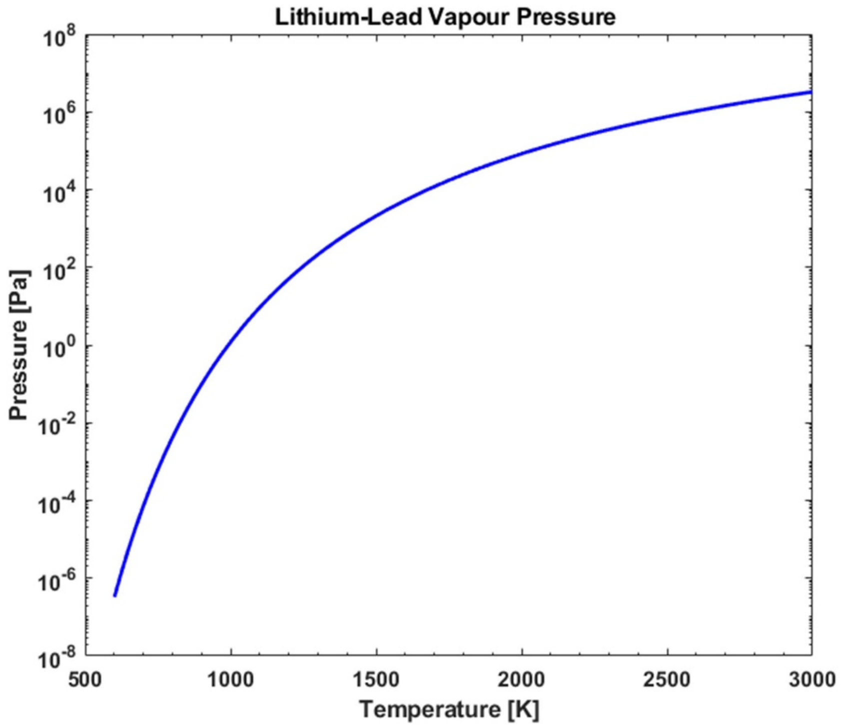

Figure 1. Lithium-lead vapor pressure curve data for the determination of the fitting constants.

The data obtained from the literature, as shown in figure 1, are significantly distant from the critical point of Lithium-Lead. While extremely high temperatures are not expected in the accident conditions to be simulated, SIMMER still requires vapor pressure values up to the critical point. Therefore, a meticulous procedure is necessary to calculate the fitting constants used by SIMMER in equation (2). The method employed involves a non-linear least squares approach with constraints at the critical point. This methodology ensures that the vapor pressure values calculated by SIMMER remain consistent even at temperatures near the critical point. The results of the fitting process are displayed in figure 2 and the fitting constants are provided in table 1.

The vapor phase EOS is, as stated before, a modified Redlich–Kwong equation which a similar form of the much more known Van der Waals equation. It is reported in equation (7) [14],

$$p_{\mathrm{Gm}} = \frac{R_{\mathrm{M}} T_{\mathrm{G}}}{v_{\mathrm{Gm}} - a_{\mathrm{G1,m}}} - \frac{a\left(T_{\mathrm{G}}\right)}{v_{\mathrm{Gm}}\left(v_{\mathrm{Gm}} + a_{\mathrm{G3,m}}\right)} \tag{7}$$

where R_{M}, T_{G}, v_{Gm} and p_{Gm} are the gas constant, the temperature, the specific volume and the pressure. Additionally, it is possible to note the constants $a_{\mathrm{G1,m}}$, $a_{\mathrm{G3,m}}$ and $a\left(T_{\mathrm{G}}\right)$ which temperature dependency is expressed in equation (8),

$$\begin{aligned} a\left(T_{\mathrm{G}}\right) &= a_{\mathrm{G2,m}} \left(\frac{T_{\mathrm{G}}}{T_{\mathrm{cr,m}}}\right)^{a_{\mathrm{G4,m}}} \quad T_{\mathrm{G}} < T_{\mathrm{cr,m}} \\ a\left(T_{\mathrm{G}}\right) &= a_{\mathrm{G2,m}} \left[1 + a_{\mathrm{G4,m}} \left(\frac{T_{\mathrm{G}}}{T_{\mathrm{cr,m}}} - 1\right)\right] T_{\mathrm{G}} \geqslant T_{\mathrm{cr,m}}. \end{aligned} \tag{8}$$

The constants $a_{\mathrm{G2,m}}$ and $a_{\mathrm{G4,m}}$, together with the constants $a_{\mathrm{G1,m}}$ and $a_{\mathrm{G3,m}}$ are calculated internally by SIMMER code. SIMMER computes these constants using the critical parameters and the condition that the critical isotherm has an inflection point. These constants are only calculated when the FFEOS option is selected, illustrating how this version of the EOS simplifies the modeling of new materials compared to the standard version, which would have required these constants as inputs during the SIMMER nodalization process.

The equation for the internal energy of the vapor is obtained using the MRK equation shown above to satisfy the thermodynamic relationship presented in equation (9),

$$\left(\frac{\partial e_{\mathrm{g}}}{\partial v_{\mathrm{g}}}\right) = T\left(\frac{\partial p_{\mathrm{g}}}{\partial T}\right)_{v_{\mathrm{g}}} - p_{\mathrm{g}}. \tag{9}$$

From equations (7) and (9), we can derive the expression for internal energy presented in equation (10) where the only unknown constant is $e^{\mathrm{D}}_{\mathrm{LiqG,M}}$, which is the internal energy of an infinitely diluted gas at the liquidus temperature. It is calculated using the Clausius–Clapeyron equation, reported in equation (12), evaluated at liquidus temperature, where the specific volume of the liquid has been neglected compared to the much higher vapor specific volume. The procedure to find $e^{\mathrm{D}}_{\mathrm{LiqG,M}}$ involves using equation (12) to find the left-hand side of equation (10) and then solving for $e^{\mathrm{D}}_{\mathrm{LiqG,M}}$, considering that $c_{\mathrm{vG,m}}$ is the heat capacity of the gas at constant volume which is an input parameter using the FFEOS and it is assumed to follow the monoatomic ideal gas law for

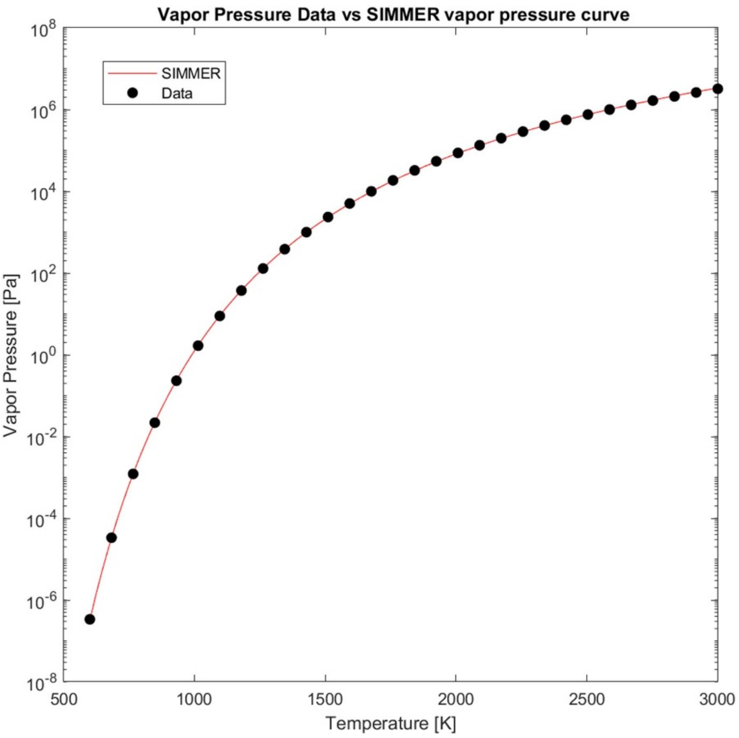

Figure 2. Vapor pressure curve comparison with SIMMER code and experimental data for lithium-lead.

Table 1. Vapor pressure SIMMER fitting constants.

SIMMER fitting constants	Value
b_{L1}	19.466 691
b_{L2}	$7.416\,831 \times 10^{-04}$
b_{L3}	$-2.448\,424 \times 10^{04}$
b_{L4}	−2.720 59

heat capacity, i.e. $c_{\mathrm{vG,m}} = 1.5R_{\mathrm{M}}$. $T_{\mathrm{Liq,M}}$ is the liquidus temperature which is again known being an input parameter of the FFEOS. Additionally, the internal energy of the saturated liquid at liquidus temperature, used in the Clausius–Clapeyron equation, equation (12), $e^{+}_{\mathrm{Liq,L,M}}$ is a FFEOS input parameter,

$$e_{\mathrm{gm}} = c_{\mathrm{vG,m}}\left(T_{\mathrm{g}} - T_{\mathrm{Liq,M}}\right) + e^{\mathrm{D}}_{\mathrm{LiqG,M}} - \frac{a_{\mathrm{G2,M}}\left(1 - a_{\mathrm{G4,M}}\right)\psi}{a_{\mathrm{G3,M}}} \ln\left(1 + \frac{a_{\mathrm{G3,M}}}{v_{\mathrm{G,M}}}\right) \tag{10}$$

where:

$$\psi = \left(\frac{T_{\mathrm{g}}}{T_{\mathrm{cr}}}\right)^{a_{\mathrm{G4,m}}} \qquad T_{\mathrm{g}} < T_{\mathrm{cr}}$$
$$\psi = 1 \qquad T_{\mathrm{g}} \geqslant T_{\mathrm{cr}} \tag{11}$$

$$e_{\mathrm{LiqG,M}} \cong e^{+}_{\mathrm{Liq,L,M}} + v^{+}_{\mathrm{g,Liq,M}}\left(T_{\mathrm{Liq,M}}\frac{\mathrm{d}p^{+}}{\mathrm{d}T}|_{\mathrm{Liq}} - p^{+}_{\mathrm{Liq,M}}\right). \tag{12}$$

The gas phase internal energy is extremely important since it is used for the evaluation of the internal energy of the liquid phase, using the Clausius–Clapeyron relation. All these state variables are determined starting from the vapor pressure curve highlighting its importance for the FFEOS model.

2.3. Lithium-lead liquid EOS

The EOS for the compressed liquid is determined starting from the saturation point of the liquid, and the effect of compressibility is accounted for by considering the difference between the actual pressure and the saturation pressure.

The SIMMER code expression is reported in equation (13)

$$v_{\mathrm{Lm}]} = v^{+}_{\mathrm{Lm}}\left\{1 - \frac{1}{\beta_{\mathrm{M}} v^{+}_{\mathrm{Lm}}}\left(\frac{\partial v_{\mathrm{Lm}}}{\partial p}\right)_{e_{\mathrm{Lm}}}\left(p - p^{+}_{\mathrm{Lm}}\right)\right\}^{-\beta_{\mathrm{M}}}. \tag{13}$$

The parameter β_{M}, is used by the code to select the form of the EOS and for lithium-lead its value is equal to −1. Therefore, the form of the EOS becomes:

$$v = v^{+}_{\mathrm{Lm}} + \left(\frac{\partial v_{\mathrm{Lm}}}{\partial p}\right)_{e_{\mathrm{Lm}}}\left(p - p^{+}_{\mathrm{Lm}}\right). \tag{14}$$

From this expression, it is clear that the specific volume of the compressed liquid consists of its saturation value, v^{+}_{Lm}, with a correction based on the difference between the actual pressure and the corresponding saturation pressure, multiplied by a factor representing the liquid's compressibility, $\left(\frac{\partial v_{\mathrm{Lm}}}{\partial p}\right)_{e_{\mathrm{Lm}}}$, i.e. the partial derivative of the specific volume with respect to pressure at constant internal energy.

In SIMMER, the saturated specific volume v^{+}_{Lm} used in equation (14) follows two analytical equations, depending on

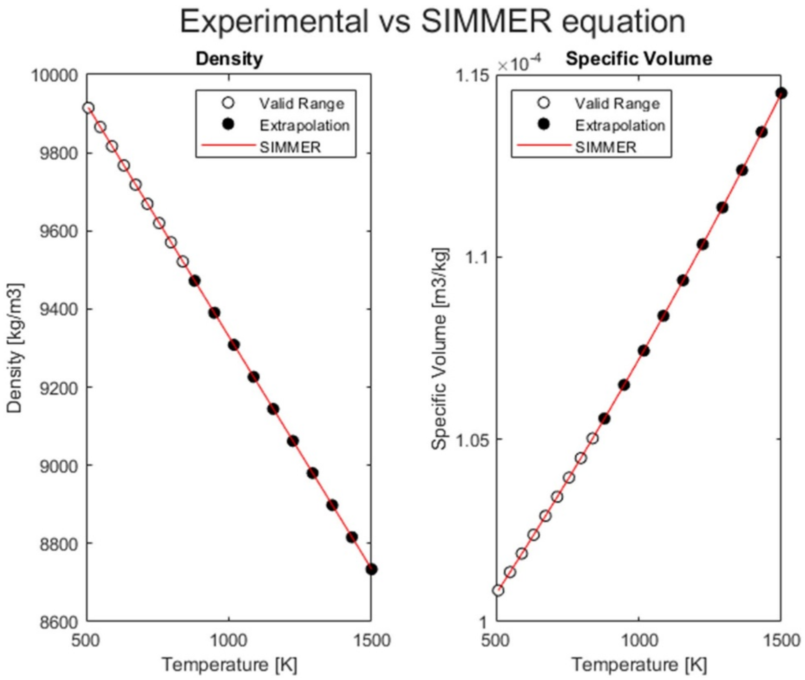

Figure 3. Specific volume and density of SIMMER analytical equation compared with experimental data for lithium-lead.

the liquid's temperature, as shown in equations (15) and (16). As the temperature approaches the critical point, a different expression for the specific volume is required to ensure consistency with the specific volume at the critical point. Additionally, while liquid metals typically exhibit a linear relationship between density and temperature at lower temperatures, near the melting point, this relationship becomes nonlinear at higher temperatures. Although such high temperatures are not expected in simulations regarding the safety of a WCLL-BB, it is still necessary to model the material accurately at those temperatures [15],

$$v_{\mathrm{Lm}}^{+} = v_{\mathrm{Liq,m}} \Big[1 + b_{\mathrm{SAT1,m}} \left(T_{\mathrm{Lm}}^{+} - T_{\mathrm{Liq,m}} \right) + b_{\mathrm{SAT2,m}} \left(T_{\mathrm{Lm}}^{+} - T_{\mathrm{Liq,m}} \right)^2 + b_{\mathrm{SAT2,m}} \left(T_{\mathrm{Lm}}^{+} - T_{\mathrm{Liq,m}} \right)^2 + b_{\mathrm{SAT3,m}} \left(T_{\mathrm{Lm}}^{+} - T_{\mathrm{Liq,m}} \right)^3 \Big]^{-1} \text{ with } T_{\mathrm{Liq,m}} \leqslant T_{\mathrm{Lm}}^{+} \leqslant b_{\mathrm{SAT4,m}} T_{\mathrm{Cr,m}} \tag{15}$$

$$v_{\mathrm{Lm}}^{+} = v_{\mathrm{Cr,m}} \left[1 + b_{\mathrm{SAT5,m}} \left(T_{\mathrm{Cr,m}} - T_{\mathrm{Lm}}^{+} \right)^{\frac{1}{2}} + b_{\mathrm{SAT6,m}} \left(T_{\mathrm{Cr,m}} - T_{\mathrm{Lm}}^{+} \right)^{2} \right]^{-1} \text{ with } b_{\mathrm{SAT4,m}} T_{\mathrm{Cr,m}} \leqslant T_{\mathrm{Lm}}^{+} \leqslant T_{\mathrm{Cr,m}}. \tag{16}$$

The coefficients $b_{\mathrm{SATi,m}}$ are the SIMMER fitting constants for the specific volume analytical function. The fitting constant in equation (15) are determined from experimental data, while the coefficients in equation (16), $b_{\mathrm{SAT5,m}}$ and $b_{\mathrm{SAT6,m}}$ are calculated internally by the code, ensuring continuity of the specific volume at the boundary temperature, $b_{\mathrm{SAT4,m}} T_{\mathrm{Cr,m}}$. SIMMER requires a boundary temperature, below which the specific volume has a linear relationship (equation (15)) with temperature, and above which it follows a polynomial expression (equation (16)). It is common practice to set the boundary temperature to 2/3 of the critical temperature.

The lithium-lead density experimental data used to obtain the coefficients $b_{\mathrm{SATi,m}}$ follows a linear relationship with temperature. The experimental data validity range is between the melting point 508 K and 880 K. The experimental data analytical expression is reported in equation (17) [16],

$$\rho = 10520.35 - 1.19051T. \tag{17}$$

Using the specific volume at the liquidus temperature, the fitting with experimental data is straightforward, and the results are presented in figure 3. Additionally, the difference between the two SIMMER equation is illustrated in figure 4 for clarity. Additionally, in table 2 are reported all the fitting constants and parameters required for the SIMMER analytical equation of the saturated specific volume, the fitting parameters $b_{\mathrm{SATi,m}}$ and specific volume at liquidus temperature, v_{LIQ} and the liquidus temperature T_{Liq}.

In relation to equation (14), the saturated liquid specific volume has been obtained above. To complete the analytical equation for the compressed liquid, determining how pressure affects the specific volume of the liquid metal is essential. This requires an expression for the partial derivative of the specific volume with respect to pressure at constant energy. The expression must be related to measurable variables, such as sound velocity, for which experimental data is available in the literature. In the case of the SIMMER code, the sound velocity of lithium-lead from published sources allows for the characterization of compressed liquid behavior, which becomes particularly important during fast transients driven by high-pressure differences, such as in the in-box LOCA scenario.

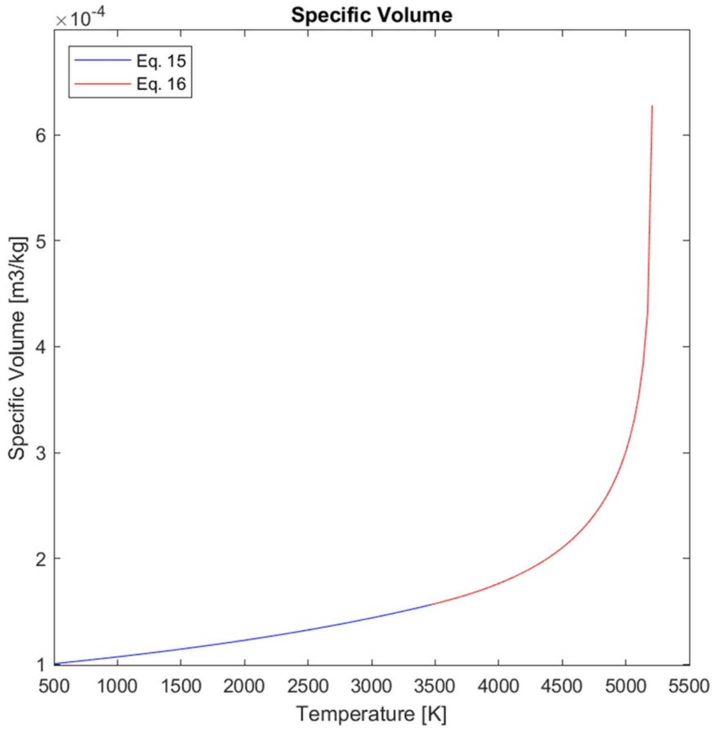

Figure 4. Specific volume of SIMMER analytical equations for all the temperature range.

Table 2. Fitting constants and parameters for lithium-lead saturated liquid specific volume EOS in SIMMER code.

SIMMER parameters	Value
$b_{\rm SAT1}$	$-1.200\,71 \times 10^{-04}$
$b_{\rm SAT2}$	0.0
$b_{\rm SAT3}$	0.0
$v_{\rm LIQ}$	$1.00\,85 \times 10^{-04}$
$T_{\rm Liq}$	508

Considering again equation (14), it is possible to relate the partial derivative of specific volume with respect to pressure at constant specific internal energy can be expressed by equation (18), which is obtained from thermodynamic relationship,

$$\left(\frac{\partial v_{\rm Lm}}{\partial p}\right)_{e_{\rm Lm}} = \left\{-\frac{1}{v_{\rm Lm}\beta_{T,\rm Lm}} - \frac{\alpha_{p,\rm Lm}}{\beta_{T,\rm Lm}}\,\frac{T_{Lm}\frac{\alpha_{p,\rm Lm}}{\beta_{T,\rm Lm}} - p}{c_{v,\rm Lm}}\right\}^{-1}. \tag{18}$$

In equation (18) the various terms are:

- $\beta_{T,\rm Lm} = -\frac{1}{v_{\rm Lm}}\left(\frac{\partial v_{\rm Lm}}{\partial p}\right)_{T_{\rm Lm}}$ the isothermal compressibility,
- $c_{\rm v,Lm} = \left(\frac{\partial e_{\rm Lm}}{\partial T}\right)_{v_{\rm Lm}}$ the heat capacity at constant volume,
- $\alpha_{\rm p,Lm} = \frac{1}{v_{\rm Lm}}\left(\frac{\partial v_{\rm Lm}}{\partial T_{\rm Lm}}\right)_p$ the volumetric thermal expansion coefficient.

The heat capacity at constant volume and the volumetric thermal expansion coefficient can be related to isothermal compressibility, which in turn can be expressed as a function of adiabatic compressibility. The latter can be related to the sound velocity. Therefore, with the FFEOS, the only required input parameters are those related to adiabatic compressibility, which can be obtained from the experimental data of the lithium-lead sound velocity. This highlights, again, the simplification of using the FFEOS compared to the standard analytical EOS, where the partial derivative in equation (14) would need to be derived using fitting constants for which finding experimental data is extremely challenging.

The SIMMER equation for the adiabatic compressibility is expressed in equation (19),

$$\beta_{\rm s,Lm} = \beta_{\rm s,LIQ,m}\left(1 + \frac{\theta}{B}\right)\left(\frac{1}{1-\theta}\right) \text{ with } \theta = \frac{T - T_{\rm LIQ,m}}{T_{\rm cr,m} - T_{\rm LIQ,m}} \tag{19}$$

where $T_{\rm LIQ,m}$ is the liquidus temperature and $T_{\rm cr,m}$ is the critical temperature. The two input parameters are $\beta_{\rm s,LIQ,m}$, which represents the adiabatic compressibility at liquidus temperature and B is a fitting constant. In equation (19) the adimensional parameter θ is used to extrapolate the adiabatic compressibility at high temperatures [17].

The adiabatic compressibility is defined in equation (20), along with its relationship to sound velocity. The speed of sound experimental relationship follows a linear relationship with temperature, decreasing as the temperature increases [16]. Its linear correlation is given in equation (21) and shown in figure 5. By using the definition of the adiabatic compressibility in equation (20) together with experimental data of the speed of sound, the experimental data of the adiabatic compressibility have been obtained. The parameters required by

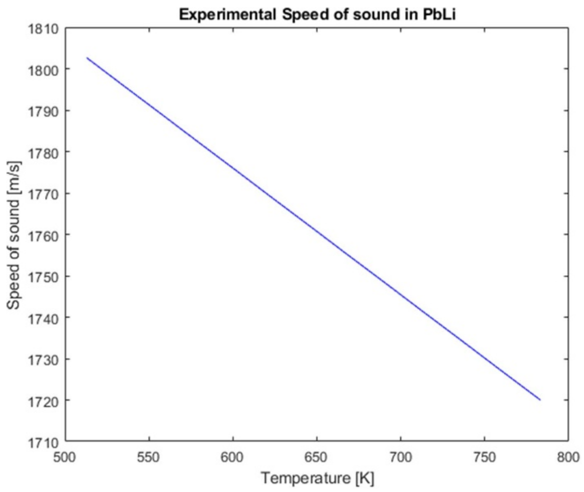

Figure 5. Experimental data of lithium-lead sound velocity.

Table 3. SIMMER parameters for lithium-lead adiabatic compressibility.

Simmer parameters	Value
$\beta_{\mathrm{s,LIQ,m}}$	3.0988×10^{-11}
B	0.8631

SIMMER have been determined fitting the obtained experimental data and the SIMMER analytical equation reported in equation (19) and are listed in table 3. Figure 6 shows the results of the fitting process. In the left graph, it is evident that the SIMMER model does not accurately reproduce experimental data at high temperatures, starting from about 2000 K. This discrepancy is due to the unreliability of high-temperature experimental data, as its valid range is from the liquidus temperature of 508 K to approximately 800 K. Although the extrapolation is not reliable at high temperatures, such conditions are not expected in any accident scenarios relevant to our study and a maximum temperature of validity of 2000 K, where difference between the SIMMER analytical equation and the experimental data begins to be large, is more than acceptable,

$$\beta_{s,\mathrm{Lm}} = -\frac{1}{v_{\mathrm{Lm}}}\left(\frac{\partial v_{\mathrm{L,m}}}{\partial p}\right)_s = \frac{1}{w_{\mathrm{sound}}^2 \rho^+} \tag{20}$$

$$w_{\mathrm{sound}} = 1876 - 0.306\,(T[\mathrm{K}] - 273.15) \tag{21}$$

Finally using this EOS, it is necessary to analyze the internal energy of liquid and its relationship with the temperature. In this version of the EOS, the liquid internal energy is evaluated as a function of temperature starting from the internal energy of the gas and using the Clausius–Clapeyron relationship. The SIMMER equation for liquid internal energy is shown in equation (22),

$$e_{\mathrm{l}} = e_{\mathrm{g}} - (v_{\mathrm{g}} - v_{\mathrm{l}})\left[T_{\mathrm{sat}}\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{sat}} - p_{\mathrm{sat}}\right] \tag{22}$$

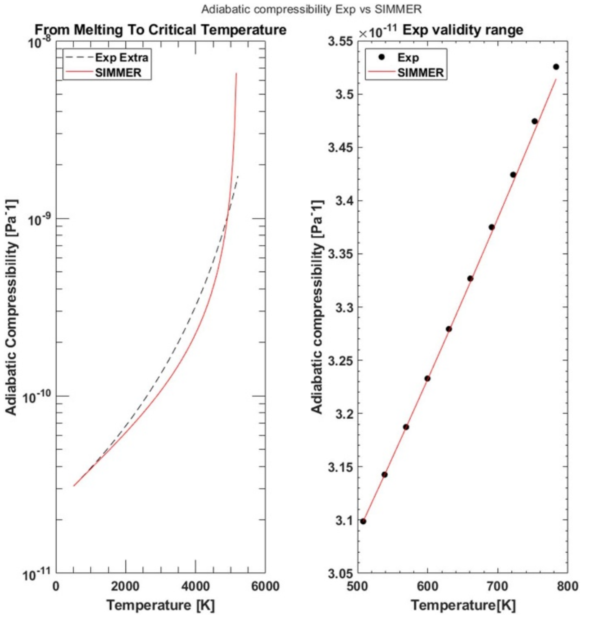

Figure 6. Adiabatic compressibility SIMMER vs experimental for the temperature validity range on the right and until the critical temperature on the left.

where:

- e_{g} is the internal energy of gas;
- v_{g} and v_{l} are the specific volume of gas and liquid;
- T_{sat} and p_{sat} are the temperature and the corresponding saturation pressure.

The internal energy of the liquid is only dependent on temperature, since the vapor pressure p_{sat} is evaluated using equation (2). Therefore, the determination of the vapor pressure curve is pivotal in obtaining a correct representation of lithium-lead liquid internal energy. It is necessary to verify that the relation between energy and temperature expressed in equation (22) is coherent and not too far from experimental data. This verification can be obtained by comparing the increase of enthalpy with temperature increase evaluated by SIMMER and the experimental enthalpy increase calculated using the specific heat measured and found in literature. The specific heat analytical form fitting the experimental data is reported in the next section and it is used to obtain the enthalpy variation reported in equation (23),

$$\Delta h = -9.906 \times 10^4 + 195\,T - 4.558 \times 10^{-3}\,T^2. \tag{23}$$

In figure 7, the comparison between the enthalpy evaluated by SIMMER and the experimental one is reported and it shows good agreement, verifying the validity of the new EOS for lithium-lead. It is important to highlight that the enthalpy is not directly used by SIMMER code whereas all the energy balance is performed with the internal energy.

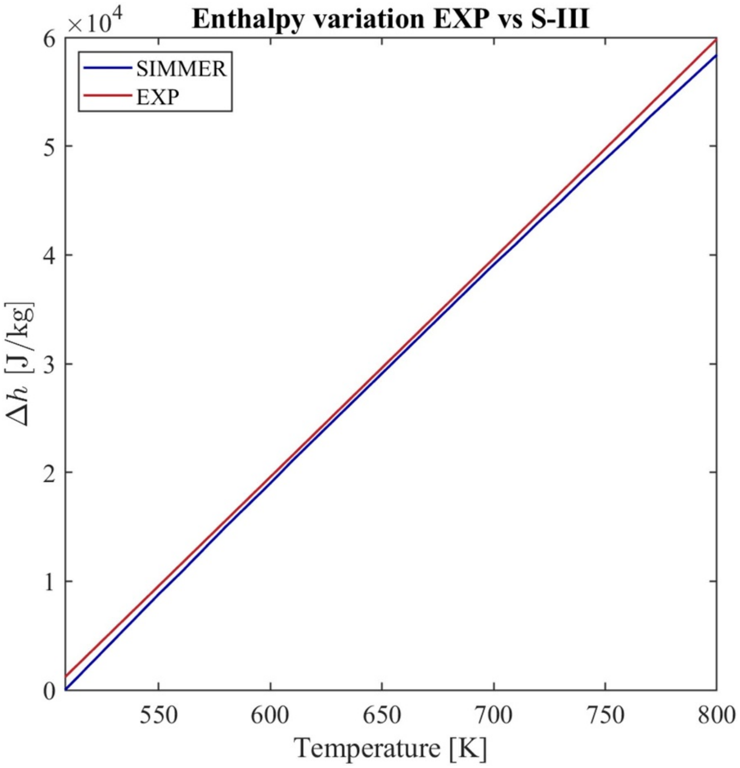

Figure 7. Comparison between the variation of enthalpy as function of energy between SIMMER EOS and experimental data.

3. Lithium-lead thermo-physical properties

The thermo-physical properties are modeled again extracting the experimental values from literature and the properties modeled for Lithium-Lead in SIMMER are [16]:

- liquid thermal conductivity,
- liquid dynamic viscosity,
- specific heat at constant pressure,
- surface tension.

The thermo-physical properties reported in [16] are usually not in the S.I. base units, however the SIMMER analytical equations are. Therefore to obtain the analytical equations it is necessary to convert the experimental data expression in S.I. base units.

The liquid thermal conductivity is obtained from literature and its relationship with temperature is given by equation (24),

$$\lambda\left[\frac{\mathrm{W}}{\mathrm{mK}^{-1}}\right]=9.14779+1.9631\times10^{-2}T[\mathrm{K}]. \tag{24}$$

SIMMER uses a second-order polynomial equation with respect to temperature, as shown in equation (25). The fitting process is straightforward, and the fitting constant is reported in table 4.

$$\kappa_{\mathrm{Lm}}=\ a_{\mathrm{k1Lm}}+a_{\mathrm{K2Lm}}T+a_{\mathrm{kL3,m}}T^2. \tag{25}$$

Table 4. SIMMER thermal conductivity fitting constants.

Simmer fitting constants	Value
a_{k1Lm}	9.147 79
a_{K2Lm}	1.9631×10^{-2}
$a_{\mathrm{kL3,m}}$	0.0

The liquid dynamic viscosity expression representing the experimental data is reported in figure 8 and it has a polynomial form and its analytical expression is given in equation (26). The SIMMER analytical function has an exponential form, and it is given by equation (27). The result of the fitting is shown in figure 8 and the SIMMER parameters are reported in table 5,

$$\mu\,[\mathrm{Pa}\cdot\mathrm{s}]=0.0061091-2.2574\times10^{-5}T+3.766\times10^{-8}T^2-2.2887\times10^{-11}T^3 \tag{26}$$

$$\mu=b_{\mathrm{ML1,m}}\exp\left(\frac{b_{\mathrm{ML2,m}}}{T}\right). \tag{27}$$

The specific heat at constant pressure, calculated using the thermophysical functions, is only used in the heat transfer routines for determining the heat transfer coefficient. In some cases, the difference between the specific heat calculated by the EOS and experimental data is significant. Therefore, the

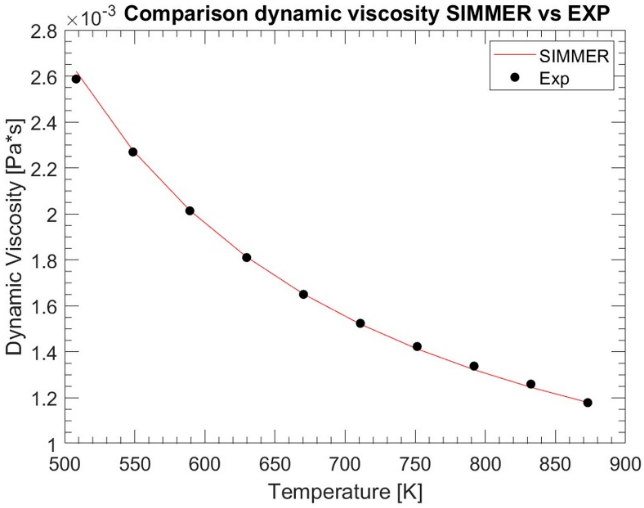

Figure 8. Lithium-lead dynamic viscosity SIMMER vs EXP.

Table 5. SIMMER fitting constants for lithium-lead dynamic viscosity.

Simmer parameters	Value
$b_{\mathrm{ML1,m}}$	$3.888\,51 \times 10^{-4}$
$b_{\mathrm{ML2,m}}$	970.0

Table 6. SIMMER fitting constants for the heat capacity at constant pressure.

Simmer parameters	Value
$d_{\mathrm{cp1,m}}$	195.0
$d_{\mathrm{cp2,m}}$	9.116×10^{-3}

specific heat found in the literature, shown in equation (28) is used to fit the SIMMER analytical function presented in equation (29),

$$c_{\mathrm{p}} = 195 - 9.116 \times 10^{-3} T[\mathrm{K}] \quad (28)$$

$$c_{\mathrm{p,Lm}} = d_{\mathrm{cp,1}} + d_{\mathrm{cp,2}} T. \quad (29)$$

The SIMMER fitting process is straightforward, and the parameters are reported in table 6.

The expression for the surface tension experimental data is given in equation (30), while in equation (31), the SIMMER analytical function for the surface tension is reported. The fitting results are shown in figure 9 and the SIMMER parameters obtained are reported in table 7.

$$\sigma = 0.4594 - 4.0 \times 10^{-5} \left(T[\mathrm{K}] - 518\right) \quad (30)$$

$$\sigma = c_{\mathrm{SL1,m}} \left(1 - \frac{T}{T_{\mathrm{cr}}}\right)^{c_{\mathrm{sL2,m}}}. \quad (31)$$

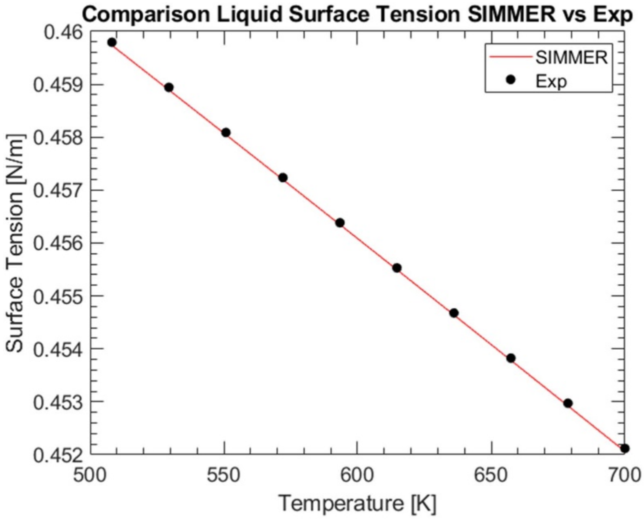

Figure 9. Lithium-lead surface tension SIMMER vs experimental.

Table 7. SIMMER fitting parameters for lithium-lead surface tension.

Simmer parameters	Value
$c_{\mathrm{sL1,m}}$	0.4792
$c_{\mathrm{sL2,m}}$	0.4039

4. Summary of EOS and TPP SIMMER variables

This brief section presents tables summarizing all modifications to the EOS and thermophysical properties. These two tables serve as standard references for creating the SIMMER input deck, replacing the previous lithium-lead properties. Table 8 lists the values for the XEOS namelist, which refers to the entries required by SIMMER for the EOS, while table 9 provides the values for the XTPP namelist which indicates the input for the thermophysical properties.

Table 8. SIMMER input parameters for XEOS namelist for lithium-lead equation of state.

S-III input deck name	Description	Value
IFREE	Activation of the FFEOS	1
IMRK	Activation of the Modified MRK	0
TCRT	Critical temperature	5208
ROCRT	Critical density	1593
TLIQUS	Liquidus temperature	508
VLIQUS	Liquidus specific volume	1.0085×10^{-4}
CVG	Specific heat at constant volume of infinitely diluted vapor	72
WM	Molecular weight	173
BL1	Fitting constant of vapor pressure curve	19.466 691
BL2	Fitting constant of vapor pressure curve	$7.416\,831 \times 10^{-04}$
BL3	Fitting constant of vapor pressure curve	$-2.448\,424 \times 10^{04}$
BL4	Fitting constant of vapor pressure curve	−2.720 59
BSAT1	Fitting constant of saturated liquid specific volume	$-1.200\,71 \times 10^{-04}$
BSAT2	Fitting constant of saturated liquid specific volume	0.0
BSAT3	Fitting constant of saturated liquid specific volume	0.0
TLBND	Boundary temperature	3472
BSL1	Adiabatic compressibility at liquidus temperature	3.0988×10^{-11}
BSL2	Fitting constant for adiabatic compressibility	0.8631
BETA	Coefficient for choosing equation for the compressed liquid	−1

Table 9. SIMMER input parameters for XTPP namelist for the thermo-physical properties of lithium-lead.

S-III Input deck Name	Description	Value
KPOPT	Flag model for conductivity	0
MUOPT	Flag model for viscosity	0
NF	Flag model for surface tension	0
CPOPT	Flag polynomial equation for specific heat at constant p	1
AKPL1	Fitting constant for thermal conductivity	9.14779
AKPL2	Fitting constant for thermal conductivity	1.9631×10^{-2}
AKPL3	Fitting constant for thermal conductivity	0.0
BMUL1	Fitting constant for dynamic viscosity	3.8851×10^{-4}
BMUL2	Fitting constant for dynamic viscosity	970.0
CSGL1	Fitting constant for surface tension	0.4792
CSGL2	Fitting constant for surface tension	0.4039
CSGL3	Minimum value allowable of surface tension	2.2992×10^{-2}
DCPL1	Fitting constant for specific heat	195
DCPL2	Fitting constant for specific heat	9.116×10^{-3}
DCPL3	Fitting constant for specific heat	0.0
DCPL4	Fitting constant for specific heat	0.0
DCPL5	Fitting constant for specific heat	0.0
DCPL6	Fitting constant for specific heat	0.0
CPLMAX	Maximum value for liquid specific heat	1.0×10^{4}
CPGMAX	Maximum value for vapor specific heat	1.0×10^{4}

5. Conclusion

This study focuses on the rigorous modeling of the thermophysical properties of lithium-lead. Prior to this work, a gap was identified in the scientific literature regarding the EOS and thermophysical properties, particularly for safety calculations involving interactions between lithium-lead and water. These scenarios require accurate relationships between the properties of the fluids involved to estimate temperature and pressure transients effectively.

In the initial phase of this work, the EOS formulations implemented in the SIMMER code were analyzed. Various types of analytical equations were detailed, with particular attention given to the FFEOS. These analytical formulations were designed to facilitate the implementation of new materials, particularly in cases where experimental data required by the standard EOS of SIMMER are unavailable. The vapor and liquid phase EOS were derived using the vapor pressure curve of lithium-lead. Since this curve is not directly available, experimental data for the individual elements comprising the liquid metal alloy were utilized. The EOS were validated against key parameters of interest, such as the temperature dependence of liquid enthalpy. The SIMMER-calculated values demonstrated acceptable discrepancies when compared with experimental data obtained through the integration of the lithium-lead specific heat. Finally, updated thermophysical properties, including thermal conductivity, dynamic viscosity, specific heat (used in heat transfer calculations), and surface tension, were derived using the most recent experimental data on lithium-lead.

In conclusion, this work addresses the need for an updated treatment of the EOS and thermophysical properties of lithium-lead. The results presented here can be considered a standard reference for safety calculations in nuclear fusion reactor designs involving lithium-lead.

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