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# Literature review of lead-lithium thermophysical properties

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# Literature review of lead-lithium thermophysical properties

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## Abstract

In recent years, the scientific community of nuclear fusion raised the issue of thermophysical properties of lead lithium alloys. These alloys are foreseen to be used in several Breeding Blanket concepts in an almost eutectic composition, but only few data on the properties are available in literature and large differences on the same property exist between different authors. Moreover, apparently each organization used different available properties correlations, making practically pointless every comparison of results with the other organizations involved in the design of Breeding Blankets. The aim of this paper is to identify the properties to be used in the design of the Breeding Blankets, performing a literature review of the available data and suggesting a correlation for each of the main properties. These correlations were chosen based on the accurateness of the paper and on the similarities between different authors, where it was possible (e.g., density). The table with the correlations should represent a starting point for a discussion to reach a general consensus on the property database, which should be mandatory in order to allow a comparison of the results from different organizations. Very likely new experiments will be necessary to definitely measure at least the properties with the biggest scattering of the data (e.g., specific heat), encouraging a consensus and reducing the errors in the design activities.

## Introduction

Lead-Lithium Eutectic (LLE) is considered as a candidate for tritium breeder and neutron multiplier in several concepts of Breeding Blankets (BB) for DEMO fusion reactor. Among the many possibilities, the alloys with a composition near the eutectic point[1] have always drawn the biggest attention, as they represent the best compromise between an acceptable tritium breeding ratio and a low lithium activity, having also the lowest melting points, an advantage for both start-up and operation.

For this reason, an accurate knowledge of and a general agreement on its thermophysical properties is essential in designing activities and to interpret the results of related experiments. In the recent years a discussion about the correlations to be used has begun among experts, given that a multiplicity of correlations properties has been used in the past activities involving the use of this alloy. Relevant discrepancies and mistakes have been found in the developed correlations. Lead-lithium alloys (PbLi) are among the most non-ideal solutions and thus it is unsatisfactory that states rules are used for the predictions of some properties. For this reason, performing new experimental activities is of outstanding importance to obtain reliable data. A literature review was already published in 2008 by Mas de les Valls et al. [32]; the section of the paper related to the thermophysical properties, however, did not provide much information about the available data and some mistakes and incorrect references were found. Therefore, an updated and extensive literature review was carried out with the aim to foster a debate among the scientific community on the accurateness of the available data and correlations.

Even if the authors are aware of the importance of the H-transport properties in the research related with tritium breeding, it was decided to leave them aside in this work, as a debate is already ongoing on the very different data obtained by different organizations and with different experimental methods [2].

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[1] a mixture of two or more component is said "eutectic" when it has the lowest crystallization temperature in the system [1].

It is probably worth giving some information on the phase diagram of PbLi before starting to deal with its properties. The eutectic title of Pb rich PbLi alloys was determined to be 15.72 at.% Li, 235°C by Hubberstey et al. [3]. Figure 1 shows the PbLi phase diagram for alloys with a Li composition between 0 and 25%. The figure shows two sets of points: the ones labelled as "present results" are the data obtained by Hubberstey et al. measuring the electrical resistance, while the ones labelled as "previous results" were extracted from the works of Czochralski et al. [4], Grube et al. [5] and Pogodin et al. [6]. The curves were drawn by least squares analysis only of the experimental data by Hubberstey et al [3]. They stated that thermal analysis method is not reliable for studying liquidus temperatures, even though it was the one that was conventionally used. Therefore, they chose to measure electrical resistance as its discontinuity allows a sharp determination of the eutectic point.

Previously to the work by Hubberstey et al. [3], the eutectic point of the PbLi system was considered to lie around 17 at.% Li and 235°C. This belief was based on the data published in the book by Hansen and Anderko [7]. The white points depicted in Figure 1 led the authors of each paper to a different eutectic point. The eutectic was found to be 16.38 at.% Li - 230°C by Czochralski et al. [4], 17 at.% Li - 235°C by Grube et al. [5], 16.35 at.% Li – 235.5°C by Pogodin et al. [6].
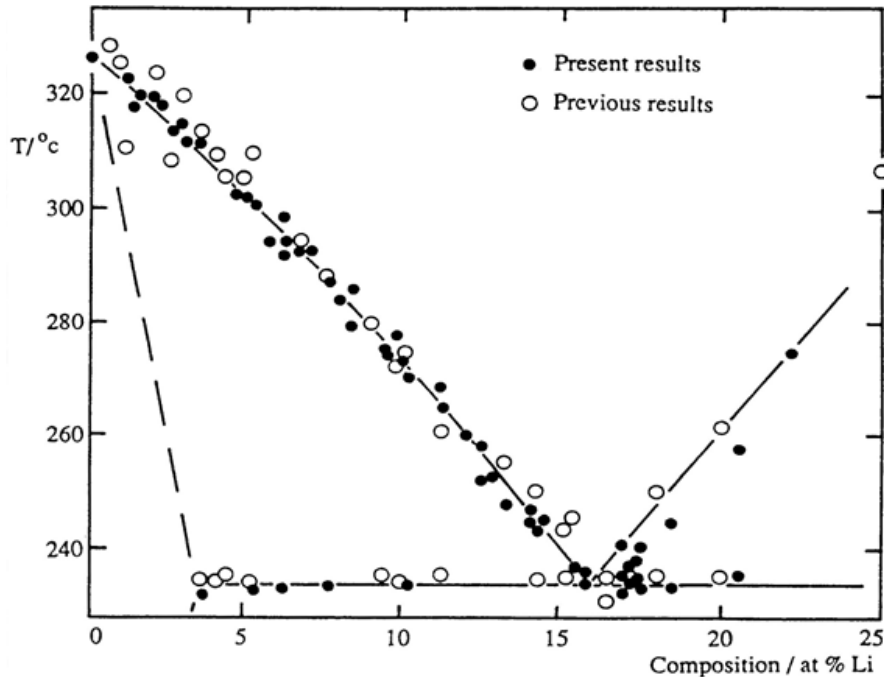


Figure 1. PbLi phase diagram between 0 and 25 at.% Li (taken from [3]).

As a separated solid phase would begin to precipitate from liquid $Pb_{83}Li_{17}$ only below 243°C [3], changing the Li content in the alloy from 17 at.% to 15.7 at.% would have a little technological impact. Moreover, a large part of the available data on many properties have been obtained for alloys with 17 at.% Li.

The first chapter of this paper suggests for each property a correlation that can be provisionally used before new data will make clearer the temperature dependence of each thermophysical property. The correlations were chosen based on the reliability of the available data and, when possible, the number of authors agreeing on similar values. The following chapters give a summary of the literature review for each property and detail only the procedure used by each author to obtain the correlation suggested in Table 1.

## Suggested correlations

Even if new experimental campaigns should be mandatory to achieve a high level of confidence on properties with the largest uncertainties, the correlations that, in the authors' opinion, could be provisionally used are listed in Table 1. The table shows the proposed correlations, the validity ranges and the scattering of correlations. With this last term, the authors mean the maximum percentage difference between each proposed correlation and the most distant among the ones available in literature for the same property. The scattering for vapour pressure is indicated as "n.a." because the difference between the available correlations is many orders of magnitude and the consequent percentage difference has not sense. Instead, the correlation by Ueki et al. [39] is the only one for the speed of sound that has been found in literature and thus scattering has no meaning in this case. Under the column "Error", the accuracy is reported when indicated in the papers. In the two cases marked with a star only the standard deviation of the experimental points was indicated in the paper as reported in the table.

Table 1. List of the proposed properties.

| Property | Expression | Range [K] | Error | Scattering | Ref. |
|---|---|---|---|---|---|
| Density [kg/m$^3$] | $\varrho(17.0\ at.\%\ Li) = 10520.35 - 1.19051 \cdot T\ [K]$ | 508-880 | 0.3% | 4.39% | [10] |
| Specific heat [J/(g·K)] | $c_p(16.8\ at.\%\ Li) = 0.195 - 9.116 \cdot 10^{-6} \cdot T\ [K]$ | 508-800 | ±3%* | 31.39% | [8,9] |
| Thermal diffusivity [cm$^2$/s] | $\alpha(17.0\ at.\%\ Li) = 3.46 \cdot 10^{-4} \cdot T[K] - 1.05 \cdot 10^{-1}$ | 508-773 | $\leq 5\cdot10^{-3}$ cm$^2$/s* | 37.35% | [21] |
| Thermal conductivity [W/(cm·K)] | $\lambda\ (17.0\ at.\%\ Li) = 0.1451 + 1.9631 \cdot 10^{-4} \cdot T\ [°C]$ | 508-873 | n.d. | 37.72% | [22] |
| Dynamic viscosity [mPa·s] | $\mu\ (16.8\ at.\%\ Li) = 0.187 \cdot exp\left(\dfrac{11640}{R \cdot T\ [K]}\right)$ | 508-625 | n.d. | 14.75% | [8,9] |
| Volumetric thermal expansion coefficient [K$^{-1}$] | $\beta(17.0\ at.\%\ Li) = (11.221 + 1.531 \cdot 10^{-3} \cdot T\ [K]) \cdot 10^{-5}$ | 508-880 | 3% | 49.41% | [10] |
| Surface tension [mN/m] | $\sigma(17.0\ at.\%\ Li) = 459.4 - 0.04 \cdot (T\ [K] - 518)$ | 508-700 | 2% | 15.08% | [34] |
| Electrical resistivity [Ω·m] | $\rho_{el}(17.0\ at.\%\ Li) = 103.33 \cdot 10^{-8} - 6.750 \cdot 10^{-11} \cdot T\ [K] + 4.180 \cdot 10^{-13} \cdot (T\ [K])^2$ | 600-800 | n.d. | 11.83% | [36] |
| Vapour pressure [mbar] | $P_V(17.0\ at.\%\ Li) = 1.4508 \cdot 10^{-59} \cdot (T\ [°C])^{20.025}$ | 508-873 | n.d. | n.a. | [22] |
| Speed of sound [m/s] | $c(17.0\ at.\%\ Li) = 1876 - 0.306 \cdot T[°C]$ | 513-783 | ±7 m/s | - | [39] |

## Density

Figure 2 shows the values of LLE density, according to the data and correlations found in literature. It is possible to roughly distinguish the correlations in two groups: the ones close to the data given by Schulz et al. [8,9] and the ones similar to the data by Stankus et al. [10]. Correlations close to that obtained by Stankus show higher values of density with respect to all the other investigated works. It has to be highlighted that these sets of correlations adopted the same measurement technique (i.e., penetrating gamma-rays). Overall, the differences between the correlation with the highest values of density (i.e., Stankus et al. [10]) and the one with the lowest values (i.e., the one labelled as IAEA-2 [16,17]) were found to be in the order of 3.16% (referred to the densities by Stankus et al.).
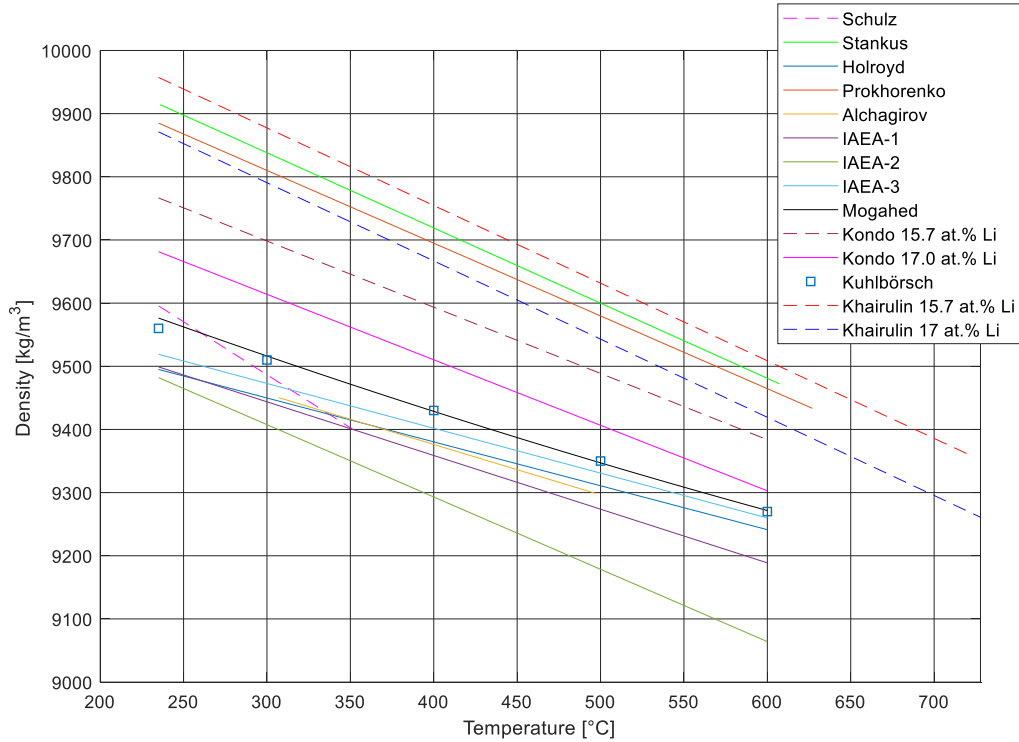
Figure 2. PbLi alloys density Vs temperature according to available references.

Table 2 shows the correlations with the first author of the related paper or technical report, whether or not the correlation is experimentally evaluated, the method used to obtain it and the temperature range of validity. An important point that has to be considered is the Li content of the PbLi alloy. Few authors report the exact composition of their alloy, among them [8,9], [10] and [11], while the others simply state that their activity was performed with LLE. For this reason, it cannot be excluded that a part of the differences between the data of different authors has to be ascribed to a different composition of the alloy.

Table 2. List of the authors with Li content, method and temperature range for density

| Label in Figure 2 | Year of publication | *Li content [%]* | Experimental | Method | Range [K] |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | Yes | Sessile drop | 508-625 |
| Stankus [10] | 2006 | 17.0 | Yes | Penetrating γ rays | 508-880 |
| Holroyd [19] | 1984 | 17.0 | No | Reference [20] | ? |
| Prokhorenko [13] | 1988 | 17.0 | Yes | Penetrating γ rays | 508-900 |
| Alchagirov [14] | 2005 | 17.0 | Yes | Pycnometric | 580-770 |
| Mogahed [22] | 1995 | 17.0 | No | References [9,23,23,24,25] | 508-873 |
| Kondo [21] | 2016 | 15.7/17.0 | No | Approximation of [15] | 673-873 |
| Kuhlbörsch [18] | 1984 | 17.0 | No | Interpolation of [12] (Max. bubble pressure) | 508-873 |
| Khairulin [11] | 2017 | 15.7 | Yes | Penetrating γ rays | 508-997 |
|  |  | 17.0 |  |  | 510-1001 |
| IAEA-1 [16, 17] | 2008 | 17.0 | No | Averaging three correlations | N.A. |
| IAEA-2 [16, 17] | 2008 | 17.0 | No | Additivity law by volume fractions | N.A. |
| IAEA-3 [16,17] | 2008 | 17.0 | No | Approximation of [12] | N.A. |

The correlation by Stankus et al. [10] was chosen for Table 1. They opened their paper with a partial literature review, exhaustively commenting the results of Schulz [8], Prokhorenko et al. [13] and Alchagirov et al. [14]. After this, the authors described in details their work: they used an alloy with 0.68 wt.% Li (about 17 at.%) and 99.32 wt.% Pb, determining an error lower than ± 0.20 wt.%. The alloy was prepared by weighing from 99.99% pure Pb and 99.8% pure Li, previously cleaned of oxides. Density was measured by gamma-rays, using $^{137}$Cs as source. Two series of experiments were performed for the liquid phase, by decreasing or increasing the temperature. The author specified that the confidence error for the liquid phase is about 0.3%. The approximating correlations, with ρ in kg/m³, are:

$$\varrho(17.0 \ at.\% \ Li) = 10534.01 - 1.20784 \ T[K] \quad \text{for the first series of data} \tag{1}$$

$$\varrho(17.0 \ at.\% \ Li) = 10504.47 - 1.17061 \ T[K] \quad \text{for the second series of data} \tag{2}$$

$$\varrho(17.0 \ at.\% \ Li) = 10520.35 - 1.19051 \ T[K] \quad \text{for both} \tag{3}$$

Only the last one of the three formulas is shown in Figure 2 to not jeopardize the legibility. The data by Stankus et al. are 3-3.5% higher than those by Schulz [8] and Alchagirov et al. [14], while they agree with those by Prokhorenko et al. [13].

**Specific heat**

Figure 3 shows the available correlations for the specific heat of lead-lithium alloys. Table 3 instead enlists the first authors of the correlations with the year of publication, the Li content, the method used to develop the correlation and the temperature validity range. In this case, the curves differ not only in the values but also in the slope. The curves labeled as Schulz, Mogahed and IAEA-2 are superimposed. Eight correlations were investigated and maximum differences in the order of 22.6 % where found.
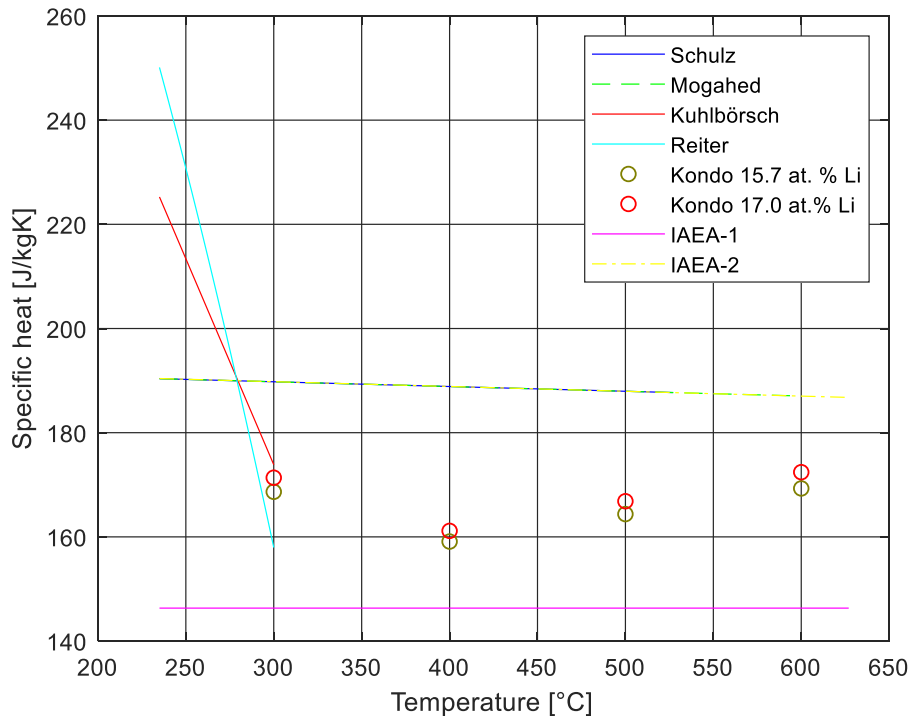


Figure 3. PbLi alloys specific heat Vs temperature according to available references.

Table 3. List of the authors with Li content, method and temperature range for specific heat.

| Label in Figure 3 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | Yes | Perkin Elmer differential scanning calorimeter | 508-800 K |
| Mogahed [22] | 1995 | 17.0 | No | References [9,18,23,24,25] | 508-873 K |
| Kuhlbörsch [18] | 1984 | 17.0 | Yes | Calvet differential calorimeter (recalibrated) | 508-573 K |
| Reiter [26] | 1982 | 17.0 | Yes | Calvet differential calorimeter | 508-573 K |
| Kondo [21] | 2016 | 15.7/17.0 | No | Rearrangement of data in [27] | 573-873 K |
| IAEA-1 [16,17] | 2008 | 17.0 | No | Additivity law by volume fractions | N.A. |
| IAEA-2 [16,17] | 2008 | 17.0 | No | Approximation of [8,9] | N.A. |

Schulz et al. [8,9], whose correlation is suggested in Table 1, prepared an alloy with a Li content of $0.67 \pm 0.01$ wt.%, corresponding to about 16.8 at.%, that was determined by atomic absorption spectroscopy. The sample preparation is described in the paper, together with the supplier and composition of pure Li and Pb. The weighing method in pure Argon was used to prepare the alloy, from Li (99.4%) and Pb (99.9%). The specific heat of solid and liquid $Pb_{83}Li_{17}$ was measured by using a Perkin Elmer differential scanning calorimeter, calibrated against a sapphire. For the liquid state, the investigated temperature range is 508 K < T < 800 K and the correlation is:

$$cp(16.8 \ at.\% \ Li) = 0.195 - 9.116{\cdot}10^{-6}{\cdot}T \ [K] \tag{4}$$

with $c_p$ expressed in J/(g·K). Two samples were tested and a standard deviation of $\pm$ 3% was highlighted. Schulz et al. [8,9] stated that other metals (e.g., Pb) and metallic alloys show a similar behaviour to $Pb_{83}Li_{17}$, with a very slight decrease with temperature (190.4 J/(g·K) at 508 K, 187.7 J/(g·K) at 800 K). Furthermore, he compared his results with those of Kuhlbörsch et al. [18] and he concluded that their results are improbable. In fact, they show a too steep decrease that would lead to $c_p$=0 if extrapolated at 800 K. Then, Schulz interpolated the data of Saar et al. [27] and found a good agreement at 1000 K, after an extrapolation of his own results.

**Thermal diffusivity**

Figure 4 shows the two correlations for thermal diffusivity found in the literature. Thermal diffusivity is here reported mostly for its importance in the calculation of the thermal conductivity performed by some authors (see the following chapter). Table 4 gives other details on the two experimental activities. As shown in Figure 4 the reported correlations show different slopes and a maximum difference in the validity range of about 37 %.
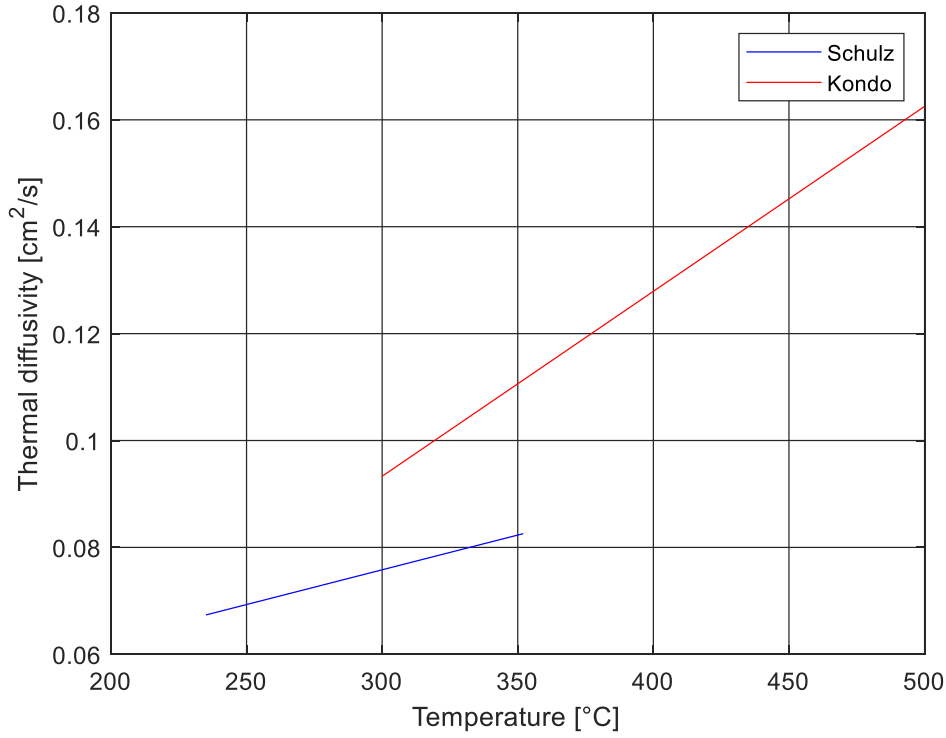
Figure 4. LLE thermal diffusivity Vs temperature according to available references.

Table 4. List of the authors with Li content, method and temperature range for thermal diffusivity.

| Label in Figure 4 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | Yes | Laser flash technique | 508-625 K |
| Kondo [21] | 2016 | 17.0 | Yes | Laser flash technique | 573-773 K |

Kondo et al. [21] measured the thermal diffusivity with the same technique of Schulz et al. [8,9], using the thermal measurement device ULVAC TC-9000. Three Li contents were examined: 5 at.%, 11 at.% and 17 at.%. This activity aimed to understand how the Li concentration would influence the thermophysical properties. Disk type samples with a diameter lower than 9 mm and a thickness of 1 mm were used and are described in detail in the paper. The samples were placed inside a graphite holder, which was located in the chamber and heated. Nd glass laser (wavelength 1.07 μm) was directed towards the top part of the capsule and the temperature change of the lower part was sampled by an infrared detector. The upper plane of the film of PbLi is heated by the laser irradiation and thus a temperature difference is created. The thermal diffusivity was evaluated by the equation:

$$\alpha = 0.1388 \cdot \frac{L^2}{t_{1/2}} \tag{5}$$

where L is the thickness of the sample and $t_{1/2}$ is the time required for the surface to reach half of the temperature rise. The tests were repeated for 10 times and the average value was taken as thermal diffusivity. Other details of the experimental procedure can be found in [21]. The $Pb_{83}Li_{17}$ samples were tested at 279, 573, 673 and 773 K. The found correlation is:

$$\alpha \left( \frac{cm^2}{s} \right) = 3.46 \cdot 10^{-4} \cdot T[K] - 1.05 \cdot 10^{-1} \tag{6}$$

## Thermal conductivity

Figure 5 shows the available correlations for thermal conductivity, while Table 5 enlists the Li content, the year of publication, the temperature range and the method used to evaluate the thermal conductivity. Seven correlations were compared for the thermal conductivity showing a mean percentage difference of about 32.06%.
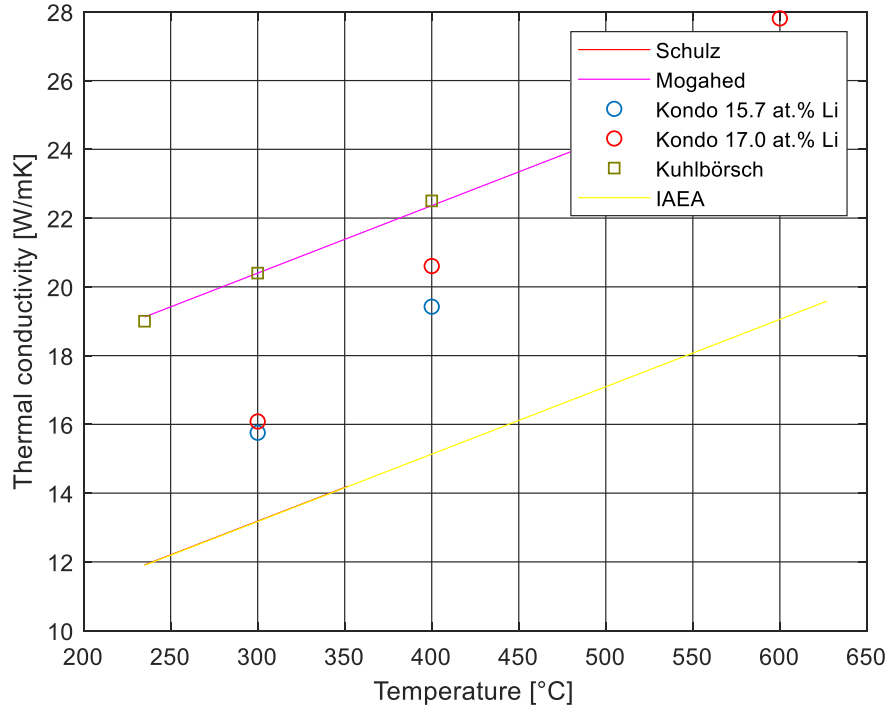


Figure 5. Figure 6. *PbLi* alloys thermal conductivity Vs temperature according to available references.

Table 5. List of the authors with *Li* content, method and temperature range for thermal conductivity.

| Label in Figure 5 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | No | Calculated from density, thermal diffusivity and specific heat | 508-625 K |
| Mogahed [22] | 1995 | 17.0 | No | References [9,18,23,24,25] | 508-873 K |
| Kuhlbörsch [18] | 1984 | 17.0 | No | Calculated by those of the pure components | 508-873 K |
| Kondo [21] | 2016 | 15.7/17.0 | No | Calculated from density, thermal diffusivity and specific heat | 573-873 K |
| IAEA [16,17] | 2008 | 17.0 | No | Approximation of [8,9] | N.A. |

The data reported by Kuhlbörsch et al. [18] were chosen as a reference, but the correlation reported in Mogahed et al. [22] has been inserted in Table 1, as it almost interpolates the data by Kuhlbörsch et al. and it is easier to be used. In their work Mogahed et al. [22] displayed several graphs for the thermophysical properties of Pb$_{83}$Li$_{17}$, among which also the thermal conductivity. As references, they cited Jauch et al. [9], Kuhlbörsch et al. [18], Hoffman et al. [23], Hultgren et al. [24] and Kardistas et al. [25]. At the moment it was not possible to find a

copy of the book by Hultgren et al. [24], while Kardistas et al. [25] referred to Schulz [8] and so to Jauch et al. [9] eventually. The paper by Hoffman et al. [23] is not clear about the source for the density values. It is likely that it takes the values from another book by Hultgren et al. [28]. In conclusion, the correlation reported by Mogahed was not found in any of the available references, but it is likely an interpolation of the experimental data by Schulz et al. [8,9] and Kuhlbörsch et al. [23]. The correlation proposed for thermal conductivity, and chosen for Table 1, is:

$$\lambda\,([\,W\,cm\cdot K]) \;=\; 0.1451 \;+\; 1.9631\,\cdot\,10^{-4}\,\cdot\,T\,[°C] \tag{6}$$

## Dynamic viscosity

The available correlations for dynamic viscosity are presented in Figure 6, Taking Schulz and IAEA-1 as references, the mean distance is $1.62\cdot10^{-4}$ Pa·s, which corresponds to the 7.12% of the values by Schulz et al. [8,9]. Maximum and minimum distances are $2.25\cdot10^{-4}$ Pa·s and $1.17\cdot10^{-4}$ Pa·s, respectively. Table 6 shows details of the activities performed by the authors of the correlation plotted.
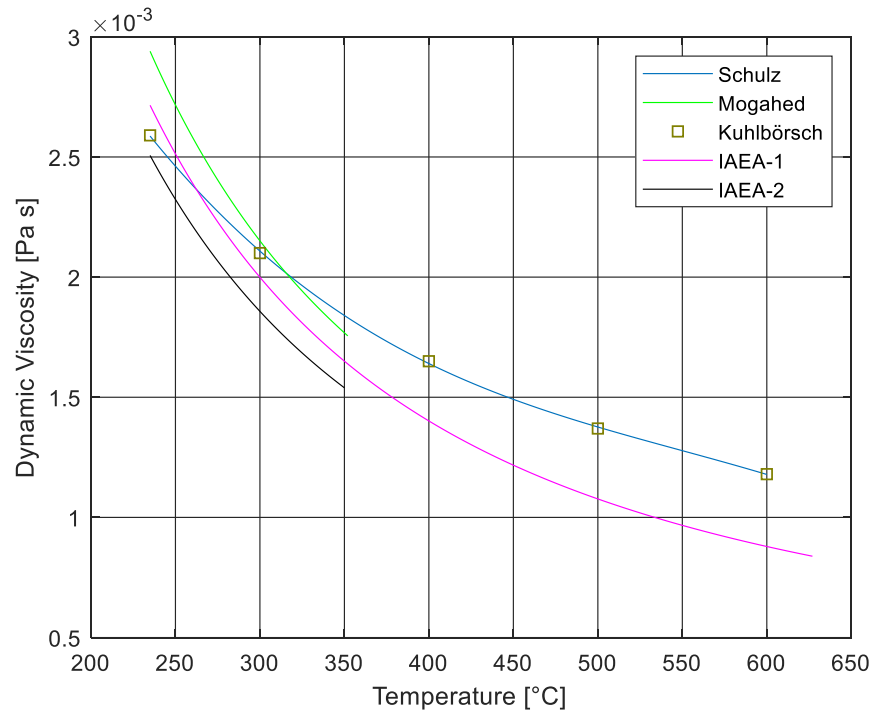


Figure 6. *PbLi* alloys dynamic viscosity Vs temperature according to available references.

Table 6. List of the authors with *Li* content, method and temperature range for dynamic viscosity.

| Label in Figure 6 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | Yes | Searle-type viscosimeter | 508-625 K |
| Mogahed [22] | 1995 | 17.0 | No | References [9,18,23,24,25] | 508-873 K |
| Kuhlbörsch [18] | 1984 | 17.0 | No | Calculated by those of the pure components | 508-873 K |
| IAEA-1 [16,17] | 2008 | 17.0 | No | Averaging two correlations | N.A. |
| IAEA-2 [16,17] | 2008 | 17.0 | No | Reference [29] | N.A. |

Schulz et al. [8,9] measured viscosity by means of a Searle-type viscometer, previously developed for metallic alloys by Schulz himself and by a Ph.D. student [30,31]. The apparatus was calibrated with standard oils. Alumina was used as material for the measuring systems. The measurements were performed under argon atmosphere. Literature data for pure lead was used for a first assessment of the accuracy of the measurement tool. The standard deviation evaluated during the tests with Pb is $\Delta\eta/\eta=\pm7\%$. The correlation proposed is valid for an alloy with 16.8 at.% Li and it is an equation of the Arrhenius type:

$$\mu\,([mPa \cdot s]) \;=\; 0.187 \cdot \exp\,(\,11640\,R \cdot T\,[K]) \tag{7}$$

where $R$ is the universal gas constant ($R$=8.314 J/(mol·K)) and 11640 J/(mol) is the activation energy (usually indicated as Q). Schulz et al. [8,9] stated that the experiments on viscosity are deeply influenced by the oxygen concentration, as lead and, especially, lithium oxides can form and thus increase the measured viscosity. Luckily, this phenomenon is highlighted by a deviation from the shape of an Arrhenius curve. However, several measurements with fresh material was performed. In the paper [8] and in the report [9], Schulz et al. made a recurrent typo on the unit of measure of the activation energy, indicating J/(mol·K) instead of J/(mol). Moreover, the paper reported a wrong formula for the generic Arrhenius equation.

## Volumetric thermal expansion coefficient

Figure 7 shows two correlations taken from literature, together with two curves derived analytically by the authors of the present paper. Two curves labeled as "Mas de les Valls" and "Stankus" are practically superimposed, while the mean distance between the curves labelled "Stankus" and "Derived analytically from [8,9]" is 5.63·10^-5 K^-1, i.e., the 31.76% of the values of the highest curve.

Table 7 shows some details on the activities performed by Mas de les Valls et al. [32] and Stankus et al. [10].
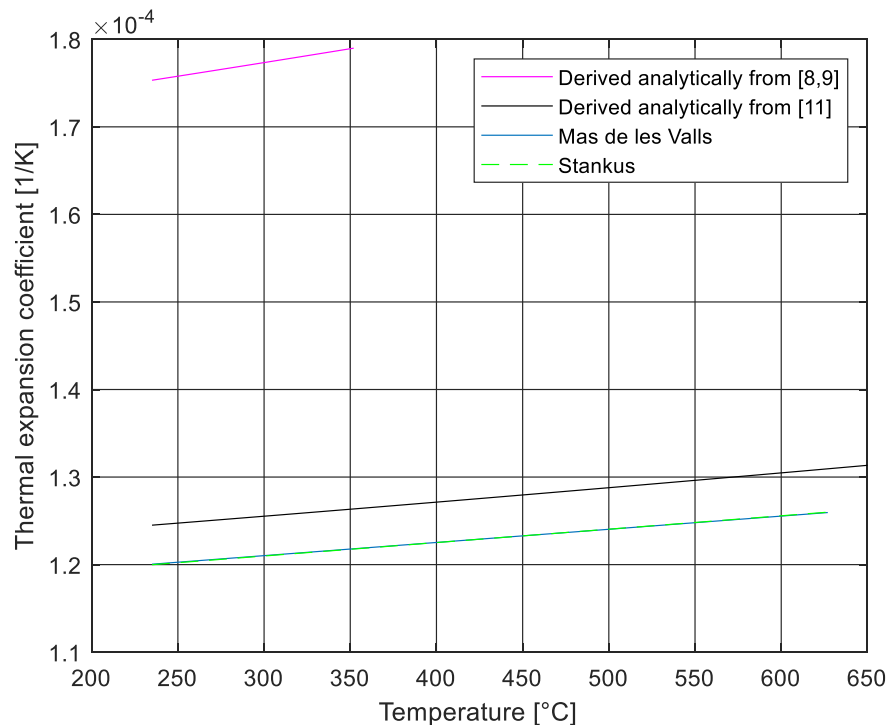


Figure 7. *PbLi* alloys volumetric thermal expansion coefficient Vs temperature according to available references.

Table 7. List of the authors with *Li* content, method and temperature range for dynamic viscosity.

| Label in Figure 7 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Mas de les Valls [32] | 2008 | 17.0 | No | References [8,10,13] | 508-880 K |
| Stankus [10] | 2006 | 17.0 | No | Calculated from the density | 360-880 K |

In particular, Stankus et al. [10] used the formula

$$\beta = -\frac{1}{\rho} \cdot \left(\frac{\partial \rho}{\partial T}\right)_p \tag{8}$$

to evaluate the volumetric thermal expansion coefficient. It has to be noted that the term $\left(\frac{\partial \rho}{\partial T}\right)_p$ is the numerical coefficient multiplied by temperature in Equations (1-3), i.e., the slope of the curve density Vs temperature. Equation (8) was evaluated with steps of 5 K. The following equation was obtained:

$$\beta([K^{-1}]) = (11.221 + 1.531 \cdot 10^{-3} \cdot T[K]) \cdot 10^{-5} \tag{9}$$

Stankus et al. [10] estimated an error of 3% for this calculation. It has to be mentioned that the generic formula (Equation (8)) reported on the paper contains an error, as it is lacking the minus sign. Moreover, the formula in Equation (9) corrects another error, as $\beta$ must be multiplied by $10^{-5}$ and not by $10^{-4}$.

With the aim to check the order of magnitude of the values calculated by Equations (9) and in the paper by Mas de les Valls et al. [32], the authors of this paper used Equation (8) to evaluate the volumetric thermal expansion coefficient starting from the density correlations from Schulz et al. [8,9] and Khairulin et al. [11]. The obtained curves are depicted in Figure 7. If the same procedure is applied at the other correlations proposed in the chapter on density, a graph with the same trends of Figure 2 but turned upside down is obtained.

## Surface tension

The available correlations on the temperature dependence of surface tension are presented in Figure 8. These correlations are in good agreement, as the mean difference between "Alchagirov" and "Mas de les Valls" is 0.0038 N/m which corresponds to 0.83% of the values of the pale blue curve. Even the correlation of Schulz, which seems far from the others, has a mean distance of 0.0143 N/m from "Alchagirov", corresponding to 3.13% of its values. Details about the depicted correlations are shown in Table 8. It is important to underline that the theory of surface phenomena of melts is under development.
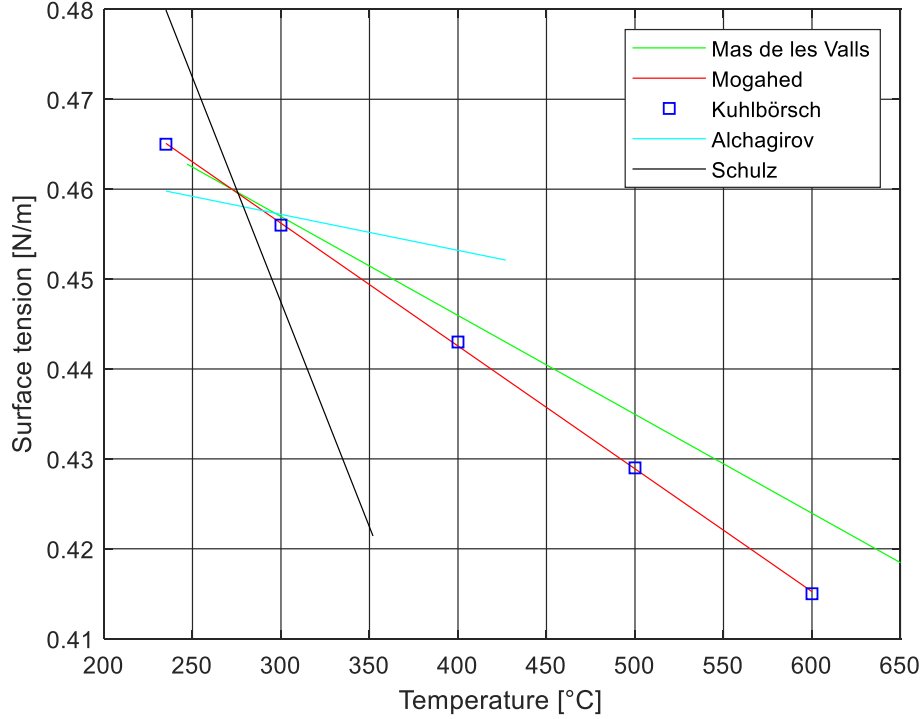
Figure 8. *PbLi* alloys surface tension Vs temperature according to available references.

Table 8. List of the authors with *Li* content, method and temperature range for surface tension.

| Label in Figure 8 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Mas de les Valls [32] | 2008 | 17.0 | No | Reference [33] | 520-1000 K |
| Mogahed [22] | 1995 | 17.0 | No | References [9,18,23,24,25] | 508-873 K |
| Kuhlbörsch [18] | 1984 | 17.0 | No | Calculated by those of the pure components | 508-873 K |
| Alchagirov [34] | 2016 | 16.87 | Yes | Large drop method | 508-700 K |
| Schulz [9] | 1986 | 16.8 | Yes | Sessile drop technique | 508-625 K |

Alchagirov et al. [34] stated to be the first to experimentally determine the surface tension of PbLi alloys with Li content up to 20 at.% and in the temperature range 508-700 K. They also pointed out that the available data about surface tension of PbLi alloys, particularly regarding significant ranges of composition and temperature, are limited. As an example, they cited the paper by Kanchukoev et al. [35], who performed analyses on alloys with a maximum of 0.3 at.% of Li. Alchagirov et al. [34] measured the surface tension with the large drop method, with an accuracy of about 2%. The special device used in this activity is described in detail in the paper, together with the experimental activity. A set of experiments with pure Pb demonstrated that the activity has the potential for a good estimation of the values of surface tension, but also highlighted a difference in the temperature coefficient, which is greater than the mean of those found in literature. 13 alloys with different Li concentrations were analysed. The correlation for 15.63 at.% and 16.87 at.% are reported hereafter:

$$\sigma([mN/m]) = 459 - 0.07 \cdot (T[K] - 553) \tag{10}$$

$$\sigma([mN/m]) = 459.4 - 0.04 \cdot (T[K] - 518) \tag{11}$$

Equation (11) is the one suggested in Table 1. If compared with equation for pure lead

$$\sigma([mN/m]) = 465.9 - 0.169 \cdot (T[K] - 600.65)$$

(12)

knowing that a reference value for lithium at the melting point is 405 mN/m, it can be noted that lithium has very low surface activity in the alloy. Alchagirov et al. [34] stated that this circumstance could be explained by the small difference between the surface tension of lead and lithium at the melting point (about 9%). Based on the low surface activity of Li, the authors also raised doubts on the reliability of the results of Kanchukoev et al. [35], giving also their explanation of the possible mistakes.

## Electrical resistivity

Figure 9 presents the available correlations for the electrical resistivity. The distance between the green and blue curves is in the range $1.17 \cdot 10^{-5}$-$1.35 \cdot 10^{-5}$ $\Omega \cdot$cm, with a mean percentage difference of 9.77% with respect to the values of "Schulz". Table 9 shows some details on the activities performed to determine the correlations.
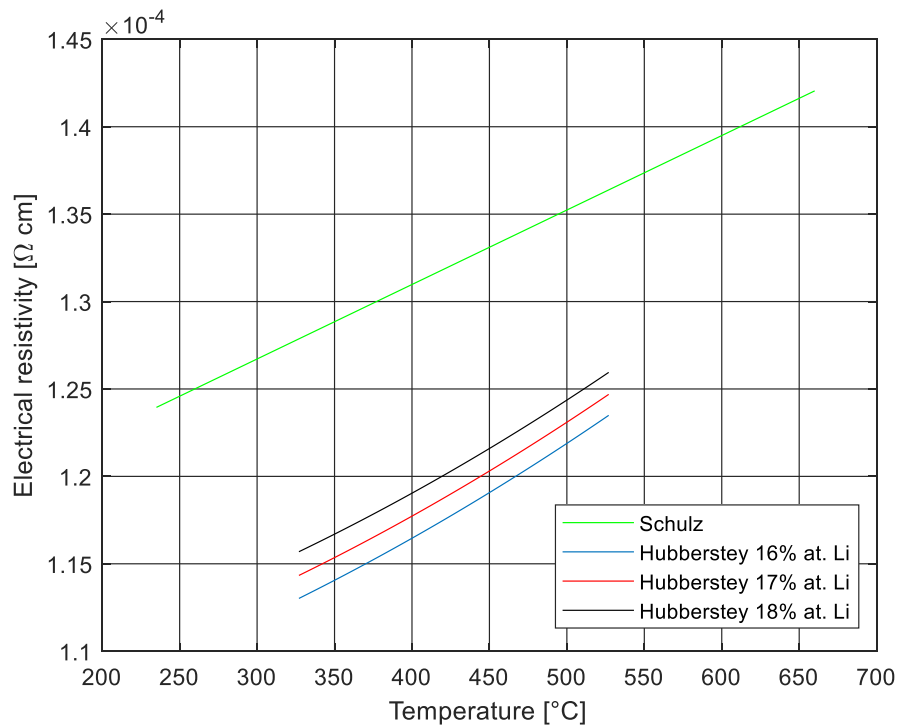


Figure 9. *PbLi* alloys electrical resistivity Vs temperature according to available references.

Table 9. List of the authors with *Li* content, method and temperature range for electrical resistivity.

| Label in Figure 9 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Schulz [8,9] | 1991 | 16.8 | Yes | Four point Thompson bridge | 508-933 K |
| Hubberstey [36] | 1991 | 16.0-17.0-18.0 | Yes | Electrical resistivity monitor | 600-800 K |

Hubberstey et al. [36] developed an electrical resistivity monitor to detect composition changes in PbLi alloys. The monitor is a development of a resistivity cell. Electrical resistivity in the ranges 600-800 K and 0-20.5 at.% Li were measured to calibrate the monitor. A positive dependence with both temperature and Li content was

highlighted. The sensitivity of the monitor is such that changes of ±0.05 at.% can be determined. The resistivity of PbLi alloys increases with the Li content up to about 80 at.%, then it decreases (Li has a lower electrical resistivity than Pb). From an analysis of an isothermal and an isocompositional curve, the authors concluded that a variation of 1 K is equivalent to a variation of 0.044 at.% Li. The correlation for resistivity as a function of temperature in the range 600-800 K is:

$$10^8 \cdot \rho([\Omega \cdot m]) = D + E \cdot T[K] + F \cdot (T[K])^2 \tag{13}$$

with the coefficient D, E and F derived from a least squares analysis of the experimental data and listed in Table 10. The same table also reported the temperature dependence coefficients calculated at 723 K. They demonstrated to be almost constant with the Li concentration in the alloy, justifying the fact that the three curves depicted in Figure 9 are parallel.

Table 10. Coefficients for Equation (13).

| $x_{Li}$ [at.% Li] | D | $10^3 \cdot E$ | $10^5 \cdot F$ | $[d\rho/dT]_{T=723 K}$ |
|---|---|---|---|---|
| 16 | 101.26 | -4.982 | 4.095 | 0.054 |
| 17 | 103.33 | -6.750 | 4.180 | 0.054 |
| 18 | 105.40 | -8.461 | 4.267 | 0.053 |

Hubberstey et al. [36] also compared their data with the study by Meijer et al. [37], who determined the resistivity of Pb, $Pb_{90}Li_{10}$, $Pb_{80}Li_{20}$ at 673 K. They found a good agreement, considering the fact that the compared data were obtained by interpolation of results presented in diagrams. Moreover, Hubberstey et al. [36] compared their results with the correlation of Schulz et al. [8,9], finding the same differences reported in the beginning of this chapter (about $13 \cdot 10^{-8}$ $\Omega \cdot m$). It has to be mentioned that Hubberstey et al. [36] stated that the correlation reported in [9] is of "unknown provenance", raising also doubts on the unit of measure to be used for temperature. However, both the paper [8] and the report [9] clearly described the experimental activity and indicated Kelvin as the chosen unit of measure for temperature.

Moreover, Schulz et al. [8,9] put on guard on the difficulty of measuring transport properties because of the high affinity of the alloy with nitrogen and oxygen. Therefore, the experiments on electrical resistivity were conducted in vacuum. However, Hubberstey et al. [36] pointed out that $Pb_{83}Li_{17}$ does not react with nitrogen and that only oxygen can alter the resistivity by lithium depletion. Moreover, neither nitrogen nor oxygen nor any other non-metals have a sufficiently high solubility in $Pb_{83}Li_{17}$ to affect resistivity as impurities. Their device is equipped with a vacuum frame through which the vessel could be evacuated, pressurized with Argon and filled with liquid metal.

## Vapour pressure

Figure 10 shows the available correlation for $Pb_{83}Li_{17}$ vapour pressure Vs temperature. It is important to recall that the vapour pressure of any substance increases non-linearly with temperature according to the Clausius-Clapeyron relation. Details on the correlations for vapour pressure can be found in Table 11. The correlations by Mogahed et al. [22], Mas de les Valls et al. [32] and the data by Kuhlbörsch et al. [18] are in good agreement, with a mean percentage difference of about 17% of the values by Mas de les Valls et al [32]. Instead, the correlation proposed in the report by IAEA [16,17] gives a completely different set of values. The mean percentage difference between it and the correlation by Mogahed is 97.1% of the values by IAEA.
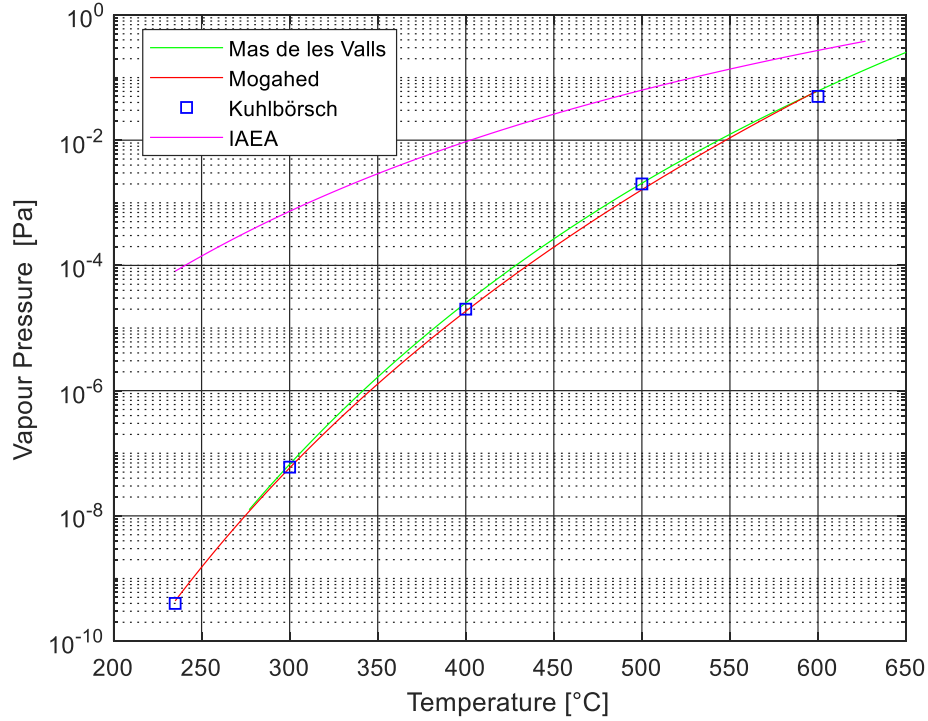
Figure 10. *PbLi* alloys vapour pressure Vs temperature according to available references.

Table 11. List of the authors with *Li* content, method and temperature range for vapour pressure.

| Label in Figure 10 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Mas de les Valls [32] | 2008 | 17.0 | No | Reference [38] | 550-1000 K |
| Mogahed [22] | 1995 | 17.0 | No | References [9,18,23,24,25] | 508-873 K |
| Kuhlbörsch [18] | 1984 | 17.0 | No | Calculated by pure components weighting on the activities | 508-873 K |
| IAEA [16,17] | 2008 | 17.0 | No | Approximation of [29] | N.A. |

As in the case of thermal conductivity, the data reported by Kuhlbörsch et al. [18] were chosen as a reference, but again the correlation reported in Mogahed et al. [22] has been inserted in Table 1 instead. The suggested correlation has been proposed for $Pb_{83}Li_{17}$, based on the same literature review explained in the chapter on thermal conductivity and states that:

$$P_V([mbar]) = 1.4508 \cdot 10^{-59} \cdot (T[°C])^{20.025} \tag{14}$$

with T expressed in °C and valid up to 600°C.

**Speed of sound**

Two references were found on $Pb_{83}Li_{17}$ speed of sound Ueki et al. [39] and Tiwari et al. [40]. The data reported in the paper by Tiwari et al. [40] were seriously flawed and consequently not reported in this paper. Figure 11 shows the correlation by Ueki et al. [39] and the results of two analytical computations performed to try to assess the reliability of the available data. Table 12 reports some details on the work by Ueki et al. [39].
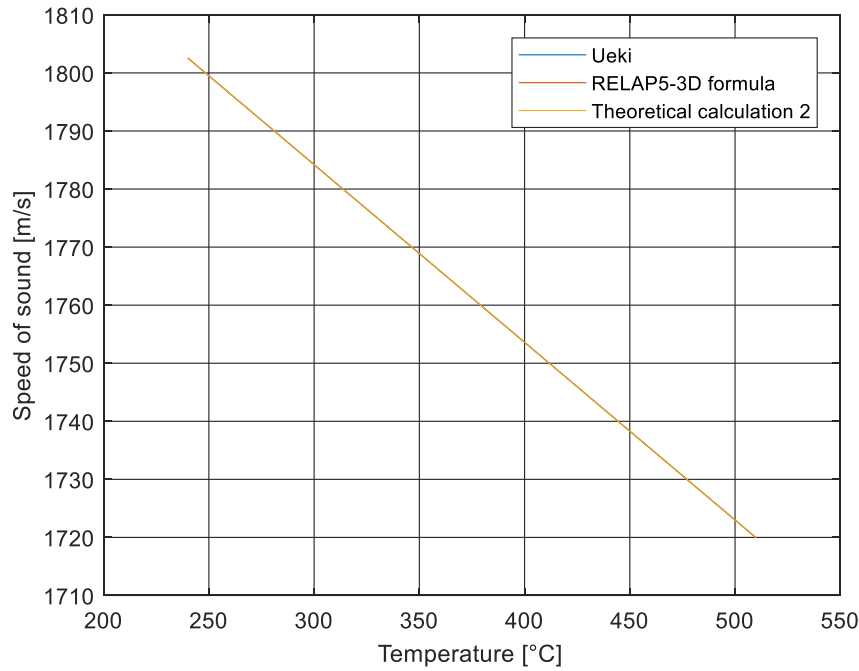
Figure 11. *PbLi* alloys speed of sound Vs temperature according to the available reference and calculated by the authors of this paper.

Table 12. List of the authors with *Li* content, method and temperature range for speed of sound.

| Label in Figure 11 | Year of publication | Li content [%] | Experimental | Method | Range |
|---|---|---|---|---|---|
| Ueki [39] | 2009 | 17.0 | Yes | Ultrasonic transmission test | 513-783 K |

Ueki et al. [39] carried out experimental activities by using pulsed ultrasonic transmission path-length between an emitter and a receiver divided by the time of flight of pulsed ultrasonic waves. The authors of the paper stated that the activity was performed for $Pb_{83}Li_{17}$. The temperature range under investigation was 513-783 K. The apparatus was calibrated with ethanol at room temperature and the speed of sound in ethanol was evaluated within 1% with respect to the reference values. It is worth mentioning that the speed of sound has a linear dependence with temperature, at the same way of lead, lead-bismuth and sodium. The proposed correlation is:

$$c([m/s]) = 1876 - 0.306 \cdot (T[°C]) \tag{15}$$

Ueki et al. [39] estimated a measurement error of ± 3 m/s. Adding the error on signal reading and on temperature, the total error proves to be ± 7 m/s.

Given that the paper by Ueki et al. [39] was the only reference found in literature, the authors of this paper performed two different analytical computations to assess its reliability. The equations used for these analyses are:

- the formula used by the system code RELAP5-3D [41] (Equation 3.2-24, pp. 186) for single-phase flow:

$$c = v \cdot \left[ \frac{\left( \frac{c_p}{T \cdot v \cdot \beta} \right)}{v \cdot \left( \beta_T \cdot \left( \frac{c_p}{T \cdot v \cdot \beta} \right) - \beta \right)} \right]^{1/2} \tag{16}$$

- the definition of speed of sound for isentropic transformations:

$$c = \sqrt{\frac{B_s}{\rho}} \tag{17}$$

where $v$ is the specific volume, $c_p$ is the specific heat, $T$ is the temperature in K, $\beta$ is the volumetric thermal expansion coefficient, $\beta_T$ is the isothermal compressibility, $\rho$ is the density and $B_s$ is the bulk modulus.

The bulk modulus was calculated with Equation (17), considering the speed of sound evaluated by Ueki et al. [39], while the isothermal compressibility was evaluated by the equation:

$$\beta_T = \frac{1}{B_s} + \frac{T \cdot \beta^2}{\rho \cdot c_p} \tag{18}$$

The correlations adopted in both calculations are:

- for density: Equation (3) by Stankus et al. [10];
- for specific heat: Equation (4) by Schulz et al. [8,9];
- for volumetric thermal expansion coefficient: Equation (9) by Stankus et al. [10].

## Conclusion

The eutectic lithium-lead alloy was proposed in the early '80s as heat carrier and tritium breeding material for fusion reactors. Since then, theoretical and experimental research activities have been conducted to determine the physical and chemical properties of LLE. However, due to the scatter of published data, the need of a detailed analysis to define a validated material database emerged especially within members of EUROfusion consortium.

As a matter of fact, the reviewed literature is affected by discrepancies about the Lithium title in the eutectic. In the paper of Hubberstey et al. [3] the authors stated that the eutectic of the lead-rich Li-Pb system is at 15.7 at.% and not at 17 at.%. Nevertheless, they clearly assert that it is not necessary to change the composition of the working fluid just to obtain the eutectic mixture in view of the extensive properties database for $Pb_{83}Li_{17}$. Presently, even if researchers seem to be oriented in the choice of the eutectic composition at 15.8 at.% Li (at least as far as the neutronic calculations are concerned [42]), no consensus between different sources has been established.

That said, the purpose of this paper was to critically analyze the documents available in literature and to propose a set of correlations to be used, in order to achieve a consensus on the properties to be used, thus allowing comparisons among different analyses and design activities.

This paper also highlighted that discrepancies still exist among the available experimental and theoretical correlations of LLE thermophysical properties. In the authors' opinion it should be mandatory to perform significant and reproducible experimental campaigns to achieve a high level of confidence at least on the properties with the largest uncertainties. A general agreement on LLE properties should be necessarily reached before to proceed with the design activities of the different blanket concepts that will employ LLE as tritium breeder.

## Acknowledgements

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