The density and thermal expansion of eutectic alloys of lead with bismuth and lithium in condensed state

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Abstract. The method of penetrating gamma-radiation is used to measure the density of lead-bismuth and lead-lithium eutectics in the condensed state in the range from room temperature to \( \sim 1250 \) K. The chemical composition of investigated eutectic alloys of Pb-Bi and Pb-Li systems is determined within \( \pm 0.2\% \) by mass, and the lead content in these alloys turns out to be 44.6 and 99.3\% by mass, respectively. The confidence error of the experimental results, which combines the systematic and random components, does not exceed 0.3\% and 0.2\% for the solid and liquid phases, respectively. The investigation results are compared with the available literature data on the density of eutectic alloys of lead with bismuth and lithium in the condensed state.

1. Introduction
The lead-bismuth eutectic is an advanced liquid-metal heat-transfer agent for transport and spaceborne fast-neutron power reactors, in particular, in strategic submarines \cite{1}, and the lead-lithium eutectic is regarded as one of the basic tritium-breeding materials of the blanket of ITER fusion reactor \cite{2}. State diagrams of these metal systems have been studied quite well \cite{3, 4}. The melting temperature \((T_m)\) of eutectic alloys of Pb–Bi and Pb–Li systems and the lead content in these systems are 398.1 and 508.1 K in accordance with the 1990 International Temperature Scale (ITS–90) \cite{5} and 44.1 and 83.0 at.\%, respectively.

In designing and developing such power plants, which operate under extreme thermal conditions, the knowledge of the thermophysical properties of their structural materials and heat-transfer agents is of great practical importance. Given in this paper are the results of experimental investigation of the density of eutectic alloys of lead with bismuth and lithium at temperatures from 293 to 1225 K; these results are used to calculate the coefficient of volumetric thermal expansion of investigated alloys in the same temperature range.

2. Current status of the problem
The experimental data available from the literature on the density of lead–bismuth and lead–lithium eutectics are given in table 1. Their confidence error was determined as a result of detailed analysis, as was done in \cite{16}, and amounted to approximately 0.5\%. However, differences are observed between the literature data, which extend beyond the limits of this error. This disagreement appears to be largely due to the difference between the chemical compositions of investigated eutectic alloys, especially in the case of the Pb–Li system, whose components are characterized by greatly differing values of density or specific volume. Therefore, the recommended reference data on the density of

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lead-bismuth and lead-lithium eutectics [17], which are based on the investigation results of different researchers given in table 1, need to be refined. For this purpose, we performed new measurements of the density of Pb–Bi and Pb–Li eutectic alloys in the condensed phase at technically important temperatures.

3. Material and method of measurements

The investigated alloys of eutectic composition were prepared by mixing from starting components under high vacuum or under low pressure of inert gas. Lead, bismuth, and lithium were 99.995, 99.985, and 99.95% by mass pure, respectively.

The method of penetrating gamma-radiation, described in detail in [18], was used for measuring the density of eutectic alloys of Pb–Bi and Pb–Li systems in the condensed state. In brief, this method consists in the following. The alloy under investigation was placed in a sealed steel ampoule and heated by an electric resistance furnace. At steady-state temperature, the alloy was irradiated by a narrow beam of γ-quanta, the source of which was provided by $^{137}$Cs isotope with an activity of 240 GBq. The density of the flux of gamma-radiation at the experimental temperature was determined by monitoring its intensity before and after its passage through the eutectic alloy in the ampoule.

Table 1. Literature data on the density of eutectic and near-eutectic alloys of Pb–Bi and Pb–Li systems in the condensed state.

| Authors, reference no., year of publication | Method of investigation | Pb content in the alloy, at.% | Temperature range of investigation, K | Number of experimental points |
|--------------------------------------------|-------------------------|-------------------------------|-------------------------------------|-------------------------------|
| Lead-bismuth eutectic                      |                         |                               |                                     |                               |
| S A Been et al., [6], 1950                  | Method of maximal pressure in gas bubble | 43.7                          | 480–1271                           | 9                             |
| N A Nikol’skiy et al., [7, 8], 1959         | Method of hydrostatic weighing | 44.7                          | 423–858                            | 17                            |
| I V Kazakova et al., [9], 1984              | Method of sessile drop    | 43.3                          | $T_m–1073$                         | –                             |
| B B Alchagirov et al., [10], 2003          | Pycnometric method       | 44.8                          | 410–727                            | 84                            |

| Lead-lithium eutectic                       |                         |                               |                                     |                               |
| H Ruppersberg and W Speicher, [11], 1976   | Method of maximal pressure in gas bubble | 80.0                          | 491–653                            | 5                             |
| B Schulz et al., [12, 13], 1986–1991       | Dilatometric method      | 83.2                          | 293–450                            | –                             |
| J Saar and H Ruppersberg, [14], 1987       | Method of sessile drop   | 80.0                          | $T_m–625$                          | 10                            |
| G M Kalinin et al., [15], 1991             | Method of maximal pressure in gas bubble | 83.0                          | 617–1083                           | –                             |
| B B Alchagirov et al., [16], 2005          | Method of penetrating gamma-radiation | 83.0                          | 293–900                            | –                             |
|                                            | Pycnometric method       | 83.0                          | 580–770                            | 115                           |
4. Measurement results and their analysis

The basic conditions of measurements of the density of lead-bismuth and lead-lithium eutectics in the condensed state are given in table 2, and the measurement results are given in figure 1. The confidence error of these experiments, which combines the systematic and random components, was 0.3% for the solid phase and 0.2% for the liquid phase.

Table 2. Basic conditions of investigation of the density of eutectic alloys of Pb–Bi and Pb–Li systems.

| Investigated alloy | Aggregate state | Thermal condition | Temperature range, K | Number of experimental points |
|--------------------|-----------------|-------------------|----------------------|------------------------------|
| Pb–Bi eutectic     | Solid phase     | Heating           | 293–$T_m$            | 2                            |
|                    | Liquid phase    | Cooling           | 1225–401             | 202                          |
| Pb–Li eutectic     | Solid phase     | Cooling           | 404–1224             | 153                          |
|                    | Liquid phase    | Heating           | 506–360              | 29                           |
|                    |                 | Heating           | 506–508              | 6                            |
|                    |                 | Cooling           | 877–524              | 47                           |
|                    |                 | Heating           | 522–880              | 44                           |

Figure 1. The temperature dependence of density of investigated eutectic alloys in the solid (●) and liquid (○) phases.

The least squares method was used for processing the experimental data obtained for the density of each one of the investigated alloys in the solid and liquid phases. A polynomial in integral powers of temperature of the form

$$\rho = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \ldots$$

was used as the approximating equation, where $\rho$ is in kg m$^{-3}$ and $T$ is in K in accordance with ITS–90.
The optimal power of approximating equation (1) was determined by regression-statistical analysis of the results of mathematical treatment using Fisher’s ratio test [19]. The coefficients of this equation are given in table 3.

**Table 3. Coefficients of approximating equation (1).**

| Investigated alloy | Aggregate state | $a_0$, kg m$^{-1}$ | $a_1$, kg m$^{-3}$ K$^{-1}$ | $a_2 \cdot 10^3$, kg m$^{-3}$ K$^{-2}$ | $a_3 \cdot 10^6$, kg m$^{-3}$ K$^{-3}$ |
|------------------|-----------------|---------------------|-----------------------------|--------------------------------|--------------------------------|
| Pb–Bi eutectic   | Solid phase     | 10521.75            | 0.46030                     | –                             | –                             |
|                  | Liquid phase    | 11136.77            | −1.69728                    | 0.45496                       | 0.12290                       |
| Pb–Li eutectic   | Solid phase     | 10681.51            | −0.82551                    | –                             | –                             |
|                  | Liquid phase    | 10520.42            | −1.19064                    | –                             | –                             |

The deviation of the results of our measurements of the density of lead-bismuth and lead-lithium eutectics ($\rho_{\text{exp}}$) from the data calculated by approximating equation (1) ($\rho_{\text{eq}}$) is given in figures 2 and 3. The mean square value of this deviation did not exceed 0.1% for the solid phase and 0.15% for the liquid phase.

Figures 4 and 5 illustrate the deviation of the experimental data of other researchers ($\rho_{\text{lit}}$) on the density of lead-bismuth and lead-lithium eutectics in the solid and liquid phases from those calculated by approximating equation (1). One can see that the results of measurements of the density of liquid eutectic alloy of Pb–Bi system, available in the literature [6, 9, 10], agree with one another and with the experimental data of the present investigation within their error of ±0.5%; it is only the relatively old data [7, 8] that differ from them to a much greater degree. The situation is somewhat different in the case of eutectic alloy of Pb–Li system (see figure 5). A discrepancy reaching 3% in the vicinity of the melting temperature is observed between the experimental data of the present study and of Kalinin et al. [15], on the one hand, and the experimental results of [12, 13, 16], on the other hand. This discrepancy is apparently caused by the differences in the chemical composition of investigated alloys. Indeed, the difference in the lead (or lithium) content in the lead-lithium eutectic within the error of its determination (±0.2% by mass) causes the variation of the density of this alloy of about 2%.

![Figure 2](imagelink)  
*Figure 2. The deviation of the experimental data of the present study on the density of eutectic alloy of Pb–Bi system in the solid (●) and liquid (○) phases from approximating equation (1).*
Figure 3. The deviation of the experimental data of the present study on the density of eutectic alloy of Pb–Li system in the solid (●) and liquid (○) phases from approximating equation (1).

Figure 4. The deviation of the experimental data of other researchers on the density of lead-bismuth eutectic in the liquid phase from approximating equation (1): (—) Been et al., (−x−) Nikol’skiy et al., (−−−) Kazakov et al., (−−−−) Alchagirov et al.
Figure 5. The deviation of the experimental data of other researchers on the density of lead-lithium eutectic in the condensed phase from approximating equation (1): (—) Schulz et al., (···) Kalinin et al., (···) Alchagirov et al.

The coefficient of volumetric thermal expansion (CVTE) of eutectic alloys of Pb–Bi and Pb–Li systems was calculated by the formula

\[ \beta = \frac{d\rho}{dT} \rho^{-1}, \]  

(2)

where \( d\rho/dT \) is the first derivative of density with respect to absolute temperature, which is determined from approximating equation (1).

The values of \( \beta \), calculated by formula (2) for each one of the phases of eutectic alloys in the investigated temperature ranges with a step of 10 K, were processed by the least squares method using the approximating equation

\[ \beta 10^5 = b_0 + b_1 T + b_2 T^2 + \ldots, \]  

(3)

where \( \beta \) is in K\(^{-1}\) and \( T \) is in K in accordance with ITS–90.

The optimal number of terms of approximating equation (3) was likewise found using Fisher’s ratio test [19]. The coefficients of this equation are given in table 4.

| Investigated alloy | Aggregate state | \( b_0 \), K\(^{-1}\) | \( b_1 \) \( 10^1 \), K\(^{-2}\) | \( b_2 \) \( 10^3 \), K\(^{-3}\) |
|-------------------|----------------|-----------------|-----------------|-----------------|
| Pb–Bi eutectic    | Solid state   | 4.372           | −0.186          | −               |
|                   | Liquid state  | 13.338          | −1.108          | 0.417           |
| Pb–Li eutectic    | Solid state   | 7.721           | 0.635           | −               |
|                   | Liquid state  | 11.221          | 1.531           | −               |
The error of calculated values of CVTE of lead-bismuth and lead-lithium eutectics in the condensed state was estimated by the errors of terms appearing in formula (2) and amounted to 5% and 3% for the solid and liquid phases, respectively.

The values of CVTE of Pb–Bi eutectic alloy were obtained by us for the first time; those of Pb–Li eutectic alloy agree within their error with the data of Kalinin et al. [15] and differ significantly from the data of [12, 13, 16], as was previously observed for the density of this alloy.

The values of density and CVTE of lead-bismuth and lead-lithium eutectics, calculated by approximating equations (1) and (3) in the range from room temperature to 1000 K with a step of 50 K, are given in table 5. In so doing, the density jump during melting $\delta \rho = (\rho_{\text{sol}} - \rho_{\text{liq}})\rho_{\text{sol}}^{-1}$ for eutectic alloys of Pb–Bi and Pb–Li systems turned out to be 1.68% and 3.38%, respectively. For example, according to the data of [20], the density jump during melting of pure lead is 3.20%.

Table 5. The density and coefficient of volumetric thermal expansion of lead-bismuth and lead-lithium eutectics in the condensed state.

| $T$, K | Pb–Bi eutectic | Pb–Li eutectic |
|-------|----------------|---------------|
|       | $\rho$, kg m$^{-3}$ | $\beta$, $10^5$, K$^{-1}$ | $\rho$, kg m$^{-3}$ | $\beta$, $10^5$, K$^{-1}$ |
| 293.15 | 10656.7 | 4.317 | 10439.5 | 7.907 |
| 300 | 10659.8 | 4.316 | 10433.9 | 7.912 |
| 350 | 10682.9 | 4.307 | 10392.6 | 7.943 |
| 398.1 (solid) | 10705.0 | 4.298 | – | – |
| 398.1 (liquid) | 10525.4 | 12.83 | – | – |
| 400 | 10522.8 | 12.83 | 10351.3 | 7.975 |
| 450 | 10453.9 | 12.76 | 10310.0 | 8.007 |
| 500 | 10386.5 | 12.68 | 10268.8 | 8.039 |
| 508.1 (solid) | – | – | 10262.1 | 8.044 |
| 508.1 (liquid) | – | – | 9915.5 | 12.00 |
| 550 | 10320.4 | 12.60 | 9865.6 | 12.06 |
| 600 | 10255.6 | 12.52 | 9806.0 | 12.14 |
| 650 | 10192.0 | 12.44 | 9746.5 | 12.22 |
| 700 | 10129.4 | 12.36 | 9687.0 | 12.29 |
| 750 | 10067.9 | 12.27 | 9627.4 | 12.37 |
| 800 | 10007.2 | 12.18 | 9567.9 | 12.45 |
| 850 | 9947.3 | 12.09 | 9508.4 | 12.52 |
| 900 | 9888.1 | 12.00 | 9448.8 | 12.60 |
| 950 | 9829.6 | 11.91 | 9389.3 | 12.68 |
| 1000 | 9771.6 | 11.81 | 9329.8 | 12.75 |

4. Conclusions
High-precision measurements were performed of the density of eutectic alloys of Pb–Bi and Pb–Li systems in the condensed phase; the measurements results were used to develop tables of recommended reference data on density and CVTE of investigated alloys at technically important temperatures, which refine the tables employed heretofore in nuclear and fusion power engineering [17].

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