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A general equation of state for dense liquid alkali metals

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Abstract

A general equation of state proposed by Parsafar and coworkers for compressed fluids is developed to compressed liquid alkali metals. According to the resulting equation of state p/ρ^2 is a linear function of ρ, where p is the pressure and ρ is the molar density. The slope and intercept of the linear equation are linearly temperature-dependent, i.e., by adjusting four temperature-independent parameters one can predict the volumetric behavior of dense molten alkali metals. The equation of state has been employed to calculate the liquid density of compressed alkali metals over a wide range of temperatures, from melting point up to 2000 K, and pressures ranging from saturated vapor pressure to 1000 bar. The agreement of the predicted results with experiment is remarkable. Also the equation of state has been used to calculate densities, isobaric expansivities, and isothermal compressibilities of liquid alkali metals in the saturation state. The linearity of bulk modulus versus pressure, common bulk modulus point, common compression factor point, linear isotherm regularity, and the linearity of inverse isobaric expansivity versus pressure for compressed liquid alkali metals has been checked by utilizing the present equation of state.

PACS: 51.30.+1; 51.35.+a; 61.25.Mv; 64.10.+h; 65.20.+w

1. Introduction

The reliable and consistent set of thermodynamic data for liquid alkali metals is of essential importance. This importance is based on their growing technical applications, due mainly to their specific advantages for high temperature applications. Liquid alkali metals act as coolant in nuclear power plants. The rapidly increasing fuel costs and need for improved thermal efficiency of power plants consequently led to an increase in the peak temperature of the cycles. Although, the thermodynamic properties of liquid alkali metals are widely investigated, there are temperature regions where accurate information does not exist. Prediction of these properties appears at present to be the only alternative to the experimental difficulties associated with their measurements.

A general equation of state for solids has been recently proposed by Parsafar and Mason [1]. The equation of state is based on expanding the internal energy and pressure in terms of density and temperature as

$$E = e_0(T) + e_1(T)\rho + e_2(T)\rho^2 + e_3(T)\rho^3 \quad (1)$$

and

$$pv^2 = A_0(T) + A_1(T)\rho + A_2(T)\rho^2, \quad (2)$$

where E is the internal energy, ρ is the molar density, T is the temperature, p is the pressure, $v = 1/\rho$ is the molar volume, and e_i and A_i are the expansion coefficients in Eqs. (1) and (2), respectively. The coefficients A_i are related to e_i with the following integral:

$$\frac{A_i(T)}{T} = C_{i+2} - (i+1)\int \frac{e_{i+1}(T)}{T^2}\,\mathrm{d}T, \quad (3)$$

where C_{i+2} is a constant of integration. For temperatures higher than the Debye temperature, the temperature-dependent coefficients, $A_i(T)$, are given as [1]

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$$A_i(T) = a_i + b_iT - C_iT\ln(T), \qquad (4)$$

where a_i and b_i are temperature-independent coefficients.

Recently, Parsafar et al. [2] have applied this equation of state to dense liquids and tested it against the experimental data for a number of fluids including nonpolar, polar, strongly hydrogen bonded, and quantum fluids. The range of applicability of the equation of state is for densities greater than the Boyle density, but without upper limit in the density or temperature. It is the purpose of this work to apply this equation of state to molten alkali metals. In comparison with ordinary fluids, alkali metals have different characteristics such as interactions via two different singlet- and triplet-type potentials and formation of molecular aggregations even at low pressures [3–5]. However, it is worth mentioning that there exist some similarities between fluid alkali metals and ordinary fluids that lead us to check the present equation of state for them. For example, liquid and gaseous metals can be treated as simple monatomic systems and like the normal fluids the law of corresponding states [6–8], equation of state [9], the law of rectilinear diameters [10,11], and the linear isotherm regularity [12] are applied to them.

2. Comparison with experiment

2.1. pv^2 versus ρ

We have used the experimental data by Vargaftik et al. [13–18] to check the relationship between pv^2 and ρ for compressed liquid alkali metals. Figs. 1–3 show the resulting curves for Li, K, and Cs, respectively, each of which at three isotherms; one near the melting point, one moderate, and one high temperature isotherm, over a wide pressure range from 100 to 1000 bar. It is seen that there is a linear relation between pv^2 and ρ, i.e., it is no need to consider the second order term in Eq. (2). Therefore, Eq. (2) is reduced to the following simpler form for liquid alkali metals:

$$pv^2 = A_0 + A_1\rho. \qquad (5)$$

The parameters A_0 and A_1 together with the R^2 values of the fit are shown in Table 1. Also, we have used the parameters A_0 and A_1 to predict the liquid density of Li, K, and Cs. The results are shown as average absolute deviation per cent in Table 1. As it is seen in Table 1, the maximum discrepancy is 0.230% and the overall average absolute deviation is 0.053%.

2.2. Temperature-dependence of A_0 and A_1

The temperature-dependence of parameters A_0 and A_1 are shown in Figs. 4 and 5, respectively, for liquid Na

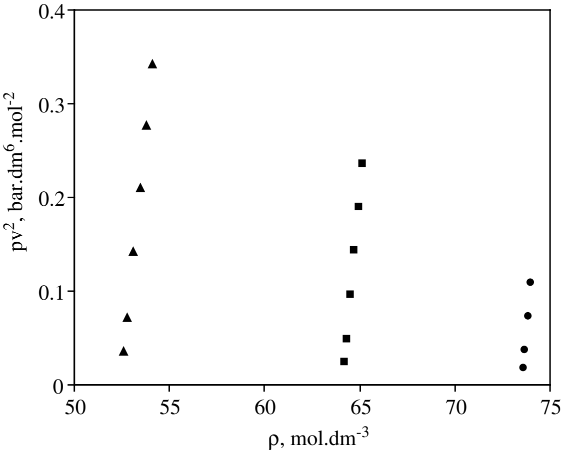

Fig. 1. Linearity of pv^2 versus ρ for Li at 500 K (●), 1200 K (■), and 2000 K (▲).

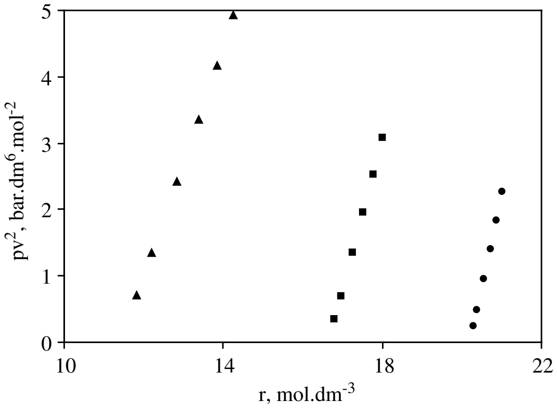

Fig. 2. The same as Fig. 1 for K at 500 K (●), 1100 K (■), and 1800 K (▲).

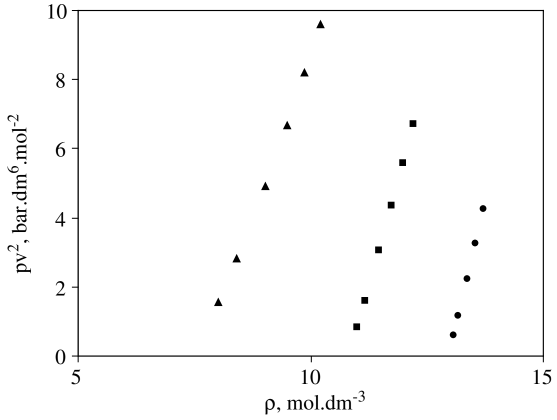

Fig. 3. The same as Fig. 1 for Cs at 500 K (●), 1000 K (■), and 1600 K (▲).

Table 1
The calculated values of the temperature-dependent parameters in Eq. (5) as a function of temperature for Li, K, and Cs

Metal	T (K)	Δp (bar)	NP	A_0 (dm^6 mol^{-2})	A_1 (dm^9 mol^{-3})	R^2	AAD (%)
Li	500	100–600	4	−17.756085	0.241429	0.999999	0.000
	1200	100–1000	6	−14.641306	0.228373	0.999998	0.000
	2000	100–1000	6	−10.756379	0.205150	0.999996	0.002
K	500	100–1000	6	−56.827739	2.811108	0.999858	0.013
	1100	100–1000	6	−37.835027	2.272362	0.999898	0.019
	1800	100–1000	6	−19.668842	1.722804	0.999550	0.100
Cs	500	100–800	5	−75.340784	5.802916	0.999761	0.023
	1000	100–1000	6	−52.636850	4.859289	0.999449	0.066
	1600	100–1000	6	−27.878374	3.654336	0.998386	0.230

The last two columns represent the coefficient of determination and the average absolute deviation percent for the calculated densities.

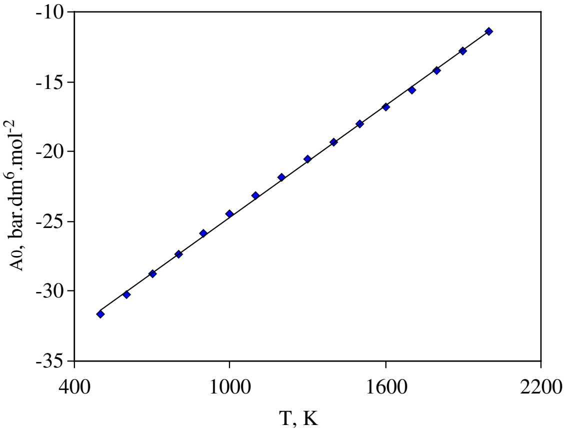

Fig. 4. Linearity of A_0 versus T. The solid line represent the beat fit through calculated values of A_0 from Eq. (5) with $R^2 = 0.9993$.

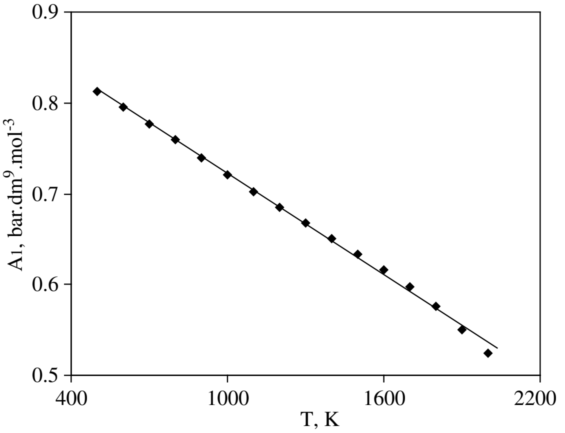

Fig. 5. The same as Fig. 4 for A_1 with $R^2 = 0.9978$.

as a typical example. It is evident that a linear equation is sufficient to describe the temperature dependencies of A_0 and A_1. The same relation exists for other liquid alkali metals. Therefore, Eq. (4) can be rewritten as the following simpler form:

$$A_i = a_i + b_i T. \tag{6}$$

We have used the experimental data [13–18] to adjust parameters a_0, b_0, a_1, and b_1. The results are shown in Table 2. The temperature-independent parameters a_0, b_0, a_1, and b_1 are employed in Eqs. (5) and (6) to calculate the liquid density of molten alkali metals. The results are shown in Table 2 as average absolute deviation and maximum deviation per cent. The agreement with experimental data is remarkable.

2.3. Saturated thermodynamic properties

Eqs. (5) and (6) have been utilized to calculate the saturated liquid densities of alkali metals. The experimental values of saturated vapor pressures [13] are used for this purpose. The deviation plots for the calculated values of saturated liquid densities of alkali metals compared with experimental values [13] are shown in Fig. 6. The agreement is quite good. We have also checked the present equation of state for the calculation of isobaric expansivities, $\alpha = -1/\rho(\partial\rho/\partial T)_p$, and isothermal compressibilities, $\beta = 1/\rho(\partial\rho/\partial p)_T$. By differentiating Eq. (5), the following equations will be obtained for α and β

$$\alpha = \frac{b_0 + b_1\rho}{2(a_0 + b_0 T) + 3(a_1 + b_1 T)\rho} \tag{7}$$

and

$$\beta = \frac{1}{2(a_0 + b_0 T)\rho^2 + 3(a_1 + b_1 T)\rho^3}. \tag{8}$$

Deviation plots for the calculated values of α and β of saturated liquid alkali metals compared with experiment [13] are shown in Figs. 7 and 8, respectively. The agreement with experimental data is good.

Table 2
Constants of Eq. (6) for alkali metals, average absolute deviation per cent, maximum deviation per cent, and the location of common bulk modulus and common compression factor points for molten alkali metals

Metal	a_0 ($\mathrm{dm^6\,mol^{-2}}$)	b_0 ($\mathrm{dm^6\,mol^{-2}\,K^{-1}}$)	a_1 ($\mathrm{dm^9\,mol^{-3}}$)	b_1 ($\mathrm{dm^9\,mol^{-3}\,K^{-1}}$)	NP	ΔT (K)	AAD (%)	MD (%)	ρ_{OB} ($\mathrm{mol\,dm^{-3}}$)	ρ_{OZ} ($\mathrm{mol\,dm^{-3}}$)
Li	−18.54024	3.762779×10^{-3}	0.232210	-1.115×10^{-5}	94	500–2000	0.02	0.08	53.23	79.84
Na	−34.99780	0.010498	0.810905	-9.058×10^{-5}	97	400–2000	0.16	1.21	28.77	43.16
K	−57.12920	0.019413	2.529596	-3.435×10^{-4}	86	400–1800	0.20	1.34	15.06	22.58
Rb	−66.91423	0.023433	3.619226	-4.783×10^{-4}	75	400–1600	0.24	1.51	12.32	18.49
Cs	−78.31023	0.028824	5.332856	-7.529×10^{-4}	74	400–1600	0.29	1.82	9.79	14.68

The pressure range is from 100 to 1000 bar.

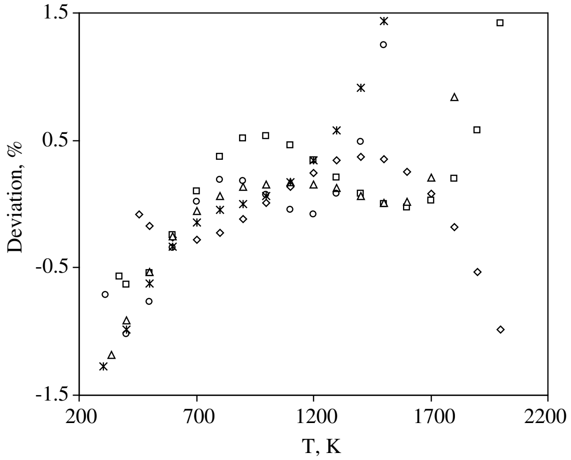

Fig. 6. Deviation plot for the predicted saturated liquid density of Li (◇), Na (□), K (△), Rb (○), and Cs (⚹) compared with experiment.

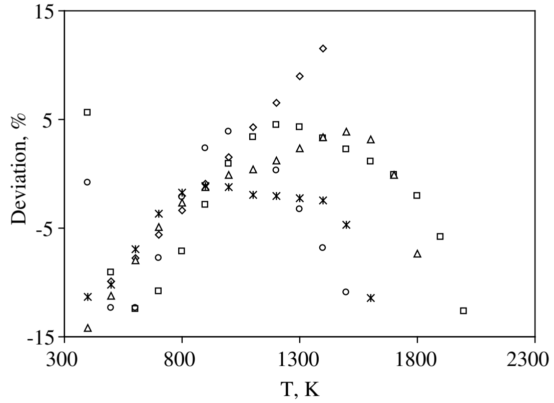

Fig. 7. The same as Fig. 6 for isobaric expansivities.

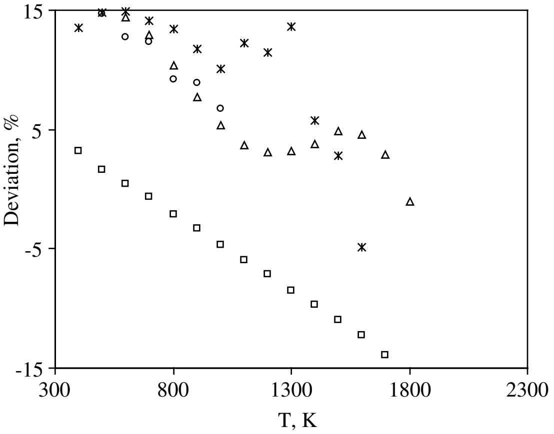

Fig. 8. Deviation plot for the calculated values of isothermal compressibilities for Na (□), K (△), Rb (○), and Cs (⚹) in the saturated state compared with experiment.

2.4. Near linearity of bulk modulus as a function of pressure

Liquids and dense fluids show a number of remarkable regularities, some of which have been known for years without any theoretical basis. Employing the present equation of state, we will examine a number of these regularities for compressed liquid alkali metals. Near linearity of bulk modulus (reciprocal isothermal compressibility), $B = \rho(\partial p/\partial \rho)_T$, of a liquid as a function of pressure was first noticed by Tait over than 100 years ago and is the basis for a number of successful equations of state for liquids [19–21]. We have examined this regularity for the present equation of state by plotting isotherms of bulk modulus for Rb, as a typical example, in Fig. 9 which shows the validity of the regularity over a wide pressure range.

2.5. Common bulk modulus point

Huang and O'Connell [22] discovered a regularity in which all isotherms of the reduced bulk modulus of a compressed liquid as a function of density intersect at a common point called 'common bulk modulus point'. The reduced bulk modulus is defined as

$$B_{\mathrm{r}} = \frac{1}{RT}\left(\frac{\partial p}{\partial \rho}\right)_T, \qquad (9)$$

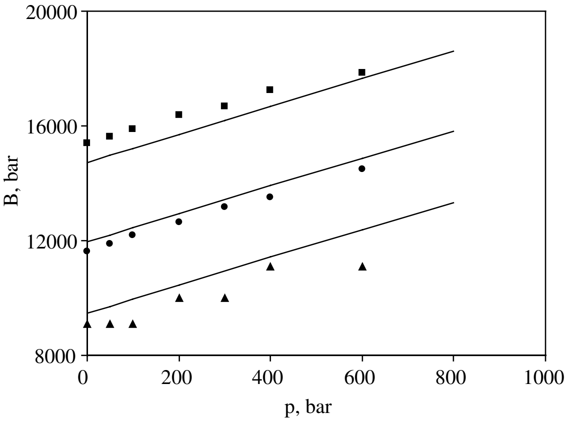

Fig. 9. Linearity of the isotherms of bulk modulus versus pressure for Rb at 500 K (■), 700 K (●), and 900 K (▲). The markers represent the experimental data and the curves are calculated values from the present equation of state.

where B_r is the reduced bulk modulus and R is the gas constant. Huang and O'Connell [22] checked the regularity for more than 250 fluids and used it as the basis of a correlation scheme for the volumetric properties of compressed liquids and liquid mixtures. Boushehri et al. [23] presented a theoretical basis for this regularity in terms of a statistical–mechanical equation of state [24].

By differentiating the present equation of state we have obtained the following equation for the reduced bulk modulus:

$$B_r = \frac{1}{RT}[2(a_0 + b_0T)\rho + 3(a_1 + b_1T)\rho^2]. \qquad (10)$$

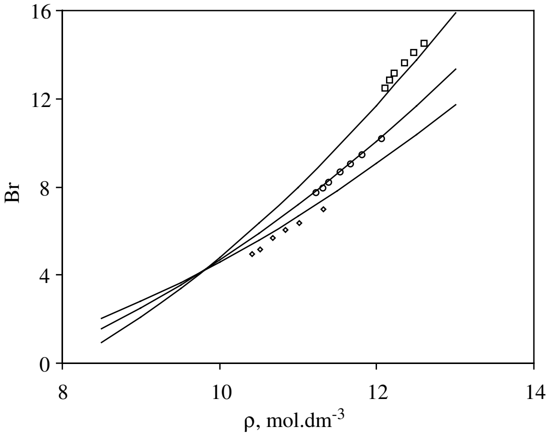

Fig. 11. The same as Fig. 9 for Cs at 700 K (□), 900 K (○), and 1100 K (◇).

We have calculated B_r for K and Cs at three isotherms. Figs. 10 and 11 show that isotherms of the reduced bulk modulus versus density intersect at a single point for K and Cs. The experimentally available data are also shown in Figs. 10 and 11. The density at the common intersection point, ρ_{OBr}, can be calculated by setting $(\partial B_r/\partial T)_\rho$ equal to zero, i.e.,

$$\rho_{\mathrm{OB_r}} = -\frac{2a_0}{3a_1}. \qquad (11)$$

The predicted values of the density at the common intersection point, by using Eq. (11), are listed in Table 2 for liquid alkali metals.

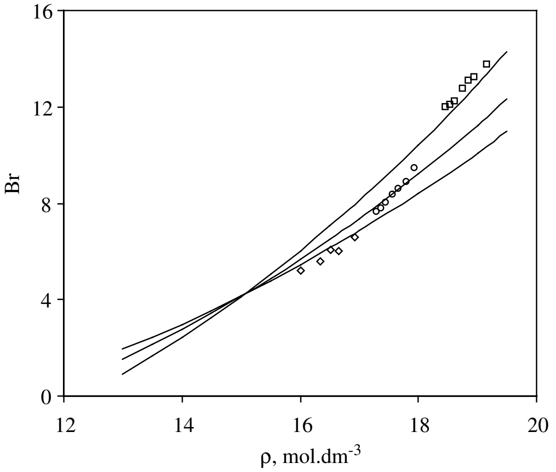

Fig. 10. Isotherms of the reduced bulk modulus versus density for K. The points are experimental data at 800 K (□), 1000 K (○), and 1200 K (◇) and the curves represent calculated values from Eq. (10).

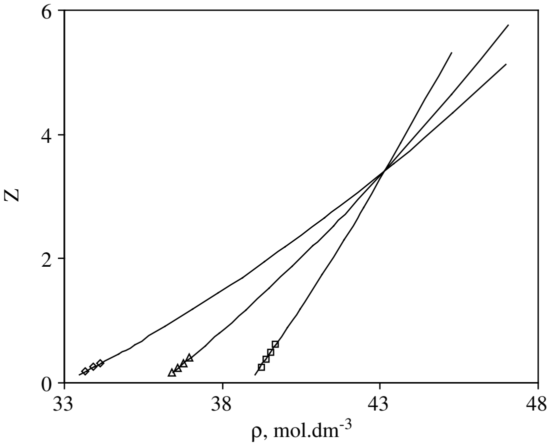

Fig. 12. Isotherms of compression factor versus density for Na. The markers represent experimental data at 500 K (□), 800 K (△), and 1100 K (◇) and the curves represent calculated values from Eq. (12).

2.6. Common compression factor point

Najafi et al. [25] showed that the isotherms of compressibility factor versus density for a dense low-temperature fluid intersect at a common point. Some of the existing equations of state such as the three-shell modifications of Lennard-Jones–Devonshire [26], linear isotherm regularity [27], the statistical–mechanical equation of state by Ihm et al. [24], and the dense system equation of state [2] show this regularity. Eq. (5) may be rearranged as follows:

$$Z = \frac{p}{\rho RT} = \frac{(a_0 + b_0 T)\rho + (a_1 + b_1 T)\rho^2}{RT}, \tag{12}$$

where Z is the compressibility factor. We have examined the present equation of state for this regularity. Fig. 12 shows the common compression factor point at three isotherms for Na. A few available experimental data are shown in Fig. 12. The density at the common intersection point, ρ_{OZ}, can be calculated by setting $(\partial Z/\partial T)_\rho$ equal to zero, which gives

$$\rho_{\mathrm{OZ}} = -\frac{a_0}{a_1}. \tag{13}$$

The calculated values of ρ_{OZ}, by using Eq. (13), for liquid alkali metals are listed in Table 2.

2.7. Linear isotherm regularity

Recently, Parsafar and Mason [27] showed that the isotherms of $(Z-1)v^2$ versus ρ^2 are linear for liquids. They have examined this regularity for a large number of fluids and called it 'linear isotherm regularity'. Ghatee et al. [12] showed that liquid alkali metals satisfy this regularity. Here, we have checked this equation of state for linear isotherm regularity against the experimental data for Li, as a typical example, in Fig. 13. The present equation of state shows the validity of this regularity in agreement with experimental data [13–18].

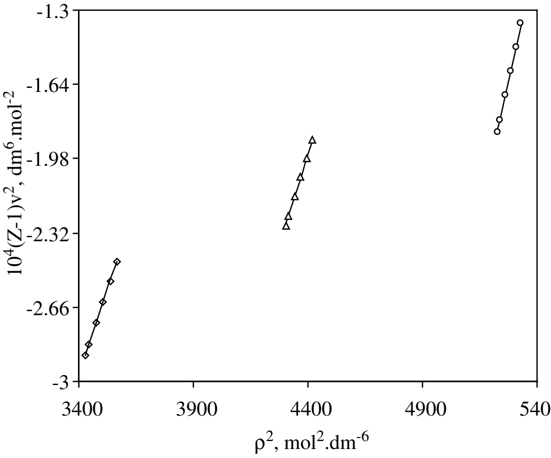

Fig. 13. Linearity of the isotherms of $(Z-1)v^2$ versus ρ^2 for Li at 600 K (○), 1100 K (△), and 1600 K (◇). The markers represent experimental data and the curves are calculated values from the present equation of state.

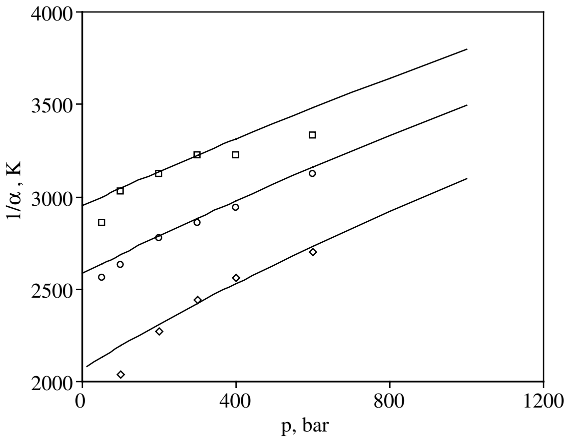

Fig. 14. Isotherms of inverse isobaric expansivity versus pressure for Rb. The points are experimental data at 800 K (□), 1000 K (○), and 1300 K (◇) and the curves represent calculated values from the present equation of state.

2.8. Near linearity of inverse isobaric expansivity as a function of pressure

Alavi et al. [28] and Boushehri and Eslami [29] showed that the isotherms of inverse isobaric expansivity versus pressure are nearly linear. In this work the present equation of state is examined for this regularity in Fig. 14 for Rb. The regularity holds over a wide pressure range for compressed liquid alkali metals.

3. Conclusion

This work shows that the original equation of state for solids [1] can be extended successfully to liquid alkali metals by performing some simplifications in its form and in its temperature-dependent parameters. Analysis of our predicted results shows that the equation of state is accurate for predicting the liquid density of molten metals over a broad temperature and pressure range. Since α and β involve differentiation of the molar density, the errors become exaggerated, of course, the resulting errors for the prediction of α and β are nearly within the experimental uncertainties. For example, the values of and β for liquid Rb at 1000 K obtained by Bystrov et al. [30] and Kozhevnikov and Karpov [31] differ by 11% and 13%, respectively.

The well-known regularities for ordinary fluids can be reproduced by the present equation of state. This fact shows that although liquid metals have different characteristics than that of ordinary fluids, they obey the same regularities. Since the structure of a dense fluid is determined primarily by the short-range repulsive forces, liquid metals like ordinary fluids obey the same regularities. The equation of state represents analytically the location of the common bulk modulus and the common compression factor intersection points. Furthermore, the ratio of $\rho_{\mathrm{OBr}}/\rho_{\mathrm{OZ}}$ obtained from the present equation of state for alkali metals is equals to 0.67, which is close to that obtained from linear isotherm regularity equation of state, 0.77, for ordinary fluids.

Finally, we have proposed a simple accurate equation of state for liquid alkali metals. The equation of state shows how the successful empirical regularities can be obtained from simple explicit expressions. Also, this work shows that to what extent the results for ordinary fluids can be extended to liquid metals.

Acknowledgements

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References

[1] G.A. Parsafar, E.A. Mason, Phys. Rev. B 49 (1994) 3049.
[2] G.A. Parsafar, N. Farzi, B. Najafi, Int. J. Thermophys. 18 (1997) 1197.
[3] C.A. Nieto de Castro, J.M.N.A. Fareleira, P.M. Matias, M.L.V. Ramires, A.A.C. Canelas, A.J.C. Varandas, Ber. Bunsenges. Phys. Chem. 94 (1990) 53.
[4] P.S. Fialho, J.M.N.A. Fareleira, M.L.V. Ramires, C.A. Nieto de Castro, Ber. Bunsenges. Phys. Chem. 97 (1993) 1487.
[5] P.S. Fialho, M.L.V. Ramires, C.A. Nieto de Castro, J.M.N.A. Fareleira, U.V. Maldorcar, Ber. Bunsenges. Phys. Chem. 98 (1994) 92.
[6] A.V. Gross, J. Inorg. Nucl. Chem. 28 (1966) 2125.
[7] H. Esalmi, Fluid Phase Equilib. 201 (2002) 57.
[8] H. Esalmi, Fluid Phase Equilib., in press.
[9] R.R. Miller, C.T. Ewing, J.R. Spann, J.P. Stone, J. Chem. Eng. Data 16 (1971) 27.
[10] F. Hensel, Chem. Bert. 5 (1988) 457.
[11] A.V. Gross, J. Inorg. Nucl. Chem. 22 (1961) 23.
[12] M.H. Ghatee, M.H. Mousazadeh, A. Boushehri, Int. J. Thermophys. 19 (1998) 317.
[13] N.B. Vargaftik, Y.K. Vinogradov, V.S. Yargin, Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures, 3rd Ed., Begell House, New York, 1996.
[14] N.B. Vargaftik, V.A. Alekseev, V.F. Kozhevnikov, Yu.F. Ryzhkov, V.G. Stepanov, Inzh.-Fiz. Zh. 35 (1978) 901.
[15] N.B. Vargaftik, V.F. Kozhevnikov, V.A. Alekseev, Inzh. Fiz. Zh. 35 (1978) 998.
[16] N.B. Vargaftik, V.F. Kozhevnikov, P.N. Ermilov, High Temp.–High Press. 16 (1984) 233.
[17] N.B. Vargaftik, V.F. Kozhevnikov, V.G. Stepanov, V.A. Alekseev, Yu.F. Ryzhkov, in: A. Cezairliyan (Ed.), Proc. 7th Symp. Thermophys. Prop., New York, 1977.
[18] N.B. Vargaftik, V.F. Kozhevnikov, P.N. Ermilov, V.A. Alekseev, in: J.V. Sengers (Ed.), Proc. 8th Symp. Thermophys. Prop., New York, 1982.
[19] A.T.J. Hayward, Br. J. Appl. Phys. 18 (1967) 965.
[20] J.R. Macdonald, Rev. Mod. Phys. 40 (1969) 316.
[21] J.H. Dymond, R. Malhorta, Int. J. Thermophys. 9 (1988) 941.
[22] Y.H. Huang, J.P. O'Connell, Fluid Phase Equilib. 37 (1987) 75.
[23] A. Boushehri, F.M. Tao, E.A. Mason, J. Phys. Chem. 97 (1993) 2711.
[24] G. Ihm, Y. Song, E.A. Mason, J. Chem. Phys. 94 (1991) 3839.
[25] B. Nagafi, G.A. Parsafar, S. Alavi, J. Phys. Chem. 99 (1995) 9248.
[26] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, 2nd Ed., Wiley, New York, 1964.
[27] G.A. Parsafar, E.A. Mason, J. Phys. Chem. 97 (1993) 9048.
[28] S. Alavi, G.A. Parsafar, B. Najafi, Int. J. Thermophys. 16 (1995) 1421.
[29] A. Boushehri, H. Eslami, Int. J. Thermophys. 18 (1997) 1027.
[30] P.L. Bystrov, D.N. Kagan, G.A. Krechetova, E.E. Shpilrain, Liquid Metal Heat Carriers for Heat Pipes and Power Facilities, Nauka, Moscow, 1988.
[31] V.F. Kozhevnikov, A.V. Karpov, Thermophysical Properties of Working Fluids and Heat Carriers of Modern Power Engineering, Moscow, 1991.