A perturbed hard-sphere-chain equation of state for liquid metals

Hossein Eslami *

Department of Chemistry, College of Sciences, Persian Gulf University, Boushehr 75168, Iran

Abstract

A perturbed hard-sphere-chain equation of state has been applied to calculate the liquid density of molten metals. Two temperature-dependent parameters appear in the equation of state, which are universal functions of the reduced temperature, i.e., two scale parameters are sufficient to calculate the temperature-dependent parameters. Generally, the scale parameters can be obtained by fitting of the experimental data. In this work we have calculated the liquid density of nine metals, including alkali metals, mercury, tin, lead, and bismuth, for which accurate experimental data exist in the literature. The calculations cover a broad range of temperatures ranging from melting point close to the critical point and at pressures ranging from the vapor-pressure curve up to pressures as high as 4000 bar. From about 800 data points examined for the aforementioned liquid metals the average absolute deviation compared with experimental data is 1.64%.

1. Introduction

Knowledge of a molecular thermodynamic model which can be suitably applied for representing volumetric and equilibrium properties of molten metals is of essential importance. Industrial applications of liquid metals in high-temperature operations such as their application in nuclear reactors, magnetohydrodynamic power generation, Rankine cycles, solar power plants, and ion propulsion systems necessitate an increasing need for knowledge of accurate volumetric and thermo-

dynamic data. Due to the difficulties associated with experimental measurements, a few experimental data are available on liquid metals, especially at very high temperatures and pressures. In these circumstances there is a growing need for an accurate theoretical model to supplement the available experimental data. It is obvious that any such model should have a statistical–mechanical basis.

In recent years the work on the prediction of properties of a system of hard-spheres has been a frequent issue of modern molecular thermodynamic theories of fluids and fluid mixtures [1–3]. The influence of the attractions and the softness of repulsions are considered as perturbations in the statistical–mechanical perturbation theories to predict the equation of state for real fluids and their mixtures. As an example of a successful

* Tel.: +98 771 454 1494; fax: +98 771 454 5188.
  E-mail address: heslami@pgu.ac.ir

statistical–mechanical analytical equation of state we may address to the equation of state derived by Song and Mason for pure fluids [4,5] and later extended to their mixtures [6,7]. This equation of state has been utilized to predict the volumetric and thermodynamic properties of a wide variety of fluids and fluid mixtures [8–11]. Previously this equation of state has been applied to liquid alkali metals in saturation [12] and compressed states [13].

The hard-sphere chain model, where a chain molecule is modeled by a series of freely jointed tangent hard spheres, is another alternative used as the reference system in statistical–mechanical perturbation theories for chain-like molecular fluids to replace much simpler hard-sphere reference system in most existing perturbation theories. Here molecular segment is a sphere of unchangeable diameter and chain molecule is a series of hard spheres. These assumptions simplify the mathematical modeling of both simple (spherical) and complex (chain-like) molecules. In 1994 Song et al. [14] proposed a perturbed hard-sphere-chain equation of state which is in better agreement with computer simulation results than those of the previous hard-sphere-chain equations of state. It is the purpose of this work to apply this equation of state to liquid metals.

2. Theory

Song et al. [14] proposed a perturbed hard-sphere-chain equation of state, which can show the behavior of long-chain molecules as well as the small ones. According to the perturbed hard-sphere-chain theory, the molecule is considered to be constituted by chains of freely jointed tangent hard bodies, or segments. This model takes into account the Chiew [15] equation of state for hard-sphere chains as the reference system and adds a van der Waals attraction term as the perturbation. The equation of state parameters are related to the intermolecular potential by the method of Song and Mason [4]. In the final form the perturbed hard-sphere-chain equation of state reads as

$$\frac{p}{\rho kT} = 1 + r^2 b \rho g(d^+) - (r-1)[g(d^+) - 1] - \frac{r^2 a \rho}{kT}, \quad (1)$$

where p is the pressure, ρ is the number (molar) density, d is the hard-sphere diameter, $g(d^+)$ is the pair radial distribution function of hard spheres at contact, and kT is the thermal energy per one molecule. Three segment-based parameters appear in Eq. (1); r is the number of segments per molecule, a reflects the attractive forces between the nonbonded segments, and b is the van der Waals covolume per segment. The analytical expression used for $g(d^+)$ is that proposed by Carnahan and Starling [16], i.e.,

$$g(d^+) = \frac{1 - \eta/2}{(1-\eta)^3}, \quad (2)$$

where η is the packing fraction defined as:

$$\eta = \frac{rb\rho}{4}. \quad (3)$$

In Eq. (1) the first three terms represent the Chiew equation of state [15] for hard spheres and the last term represents the perturbation term. The parameter b is a function of the hard sphere diameter through the following expression:

$$b(T) = 2\pi \int_0^\sigma \left[1 - \left(1 + \frac{u_0}{kT} \right) \exp(-u_0/kT) \right] R^2 \, dR, \quad (4)$$

where R is the separation distance between segment centers, $u_0(R)$ is the repulsive branch of the potential energy function, $u(R)$, and σ indicates the location of minimum in $u(R)$. The parameter a is related to the second virial coefficient, B, and the van der Waals covolume, b, as:

$$B(T) = b - \frac{a}{kT} = 2\pi \int_0^\infty [1 - \exp(-u/kT)] R^2 \, dR. \quad (5)$$

According to Eqs. (4) and (5) the knowledge of intermolecular pair potential energy function is required to obtain the temperature-dependent parameters of the equation of state, but this is seldom accurately known for most physical systems of interest. It is shown that [5] the temperature-dependent parameters, $a(T)$ and $b(T)$, are insensitive to the details of the potential energy function and when scaled in terms of suitable reducing constants, they are universal function of the reduced temperature. Therefore the parameters a and b can be written as [14]

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(kT/\varepsilon) \quad (6)$$

and

$$b(T) = \frac{2\pi}{3} \sigma^3 F_b(kT/\varepsilon), \quad (7)$$

where ε is the depth of minimum in potential energy curve and F_a and F_b are universal functions of the reduced temperature. F_a and F_b can be written as the following empirical formula [17]:

$$F_a(kT/\varepsilon) = a_1 \exp\left(-a_2 \frac{kT}{\varepsilon} \right) + a_3 \exp\left[-a_4 \left(\frac{kT}{\varepsilon} \right)^{3/2} \right] \quad (8)$$

and

$$F_b(kT/\varepsilon) = b_1 \exp\left(-b_2 \frac{kT}{\varepsilon} \right) + b_3 \exp\left[-b_4 \left(\frac{kT}{\varepsilon} \right)^{3/2} \right], \quad (9)$$

where the coefficients a_i and b_i are determined by fitting. Generally, the universal functions F_a and F_b are calculated by fitting of the experimental pvT data of a simple

fluid like Ar, for which $r = 1$. In this work we have utilized this equation of state to calculate liquid density of molten metals including alkali metals, mercury, tin, lead, and bismuth.

3. Results and discussion

As it is mentioned in the previous section, the temperature-dependent parameters of the equation of state, a and b, can be calculated by knowing the full potential energy curve, or more simply, using the empirical formula presented by Song and Mason [17]. For ordinary fluids, the constants in Eqs. (8) and (9) for F_a and F_b are fitted to the experimental data for a fluid like Ar, for which $r = 1$. Once this is performed, the equation of state is applicable to other fluids by adjusting three parameters, ε, σ, and r.

Fluid alkali metals are examples of systems interacting via two potential types. In fact they can interact through singlet- and triplet-type potentials [18–20]. This fact complicates the calculation of temperature-dependent parameters of the equation of state via knowing the potential energy function, Eqs. (4) and (5), or consequently the empirical formula by Song and Mason [17] fitted for Ar. In this work we have adapted the same mathematical form for parameters F_a and F_b as proposed by Song and Mason [17], Eqs. (8) and (9), but the coefficients a_i and b_i have been calculated using the experimental data for alkali metals. In other words, the effect of interaction via singlet- and triplet-type potentials is taken in to account in an average way as a mean spherical potential. All metallic systems are considered as monatomic systems, $r = 1$. Therefore, knowing two adjustable parameters ε and σ are sufficient to predict the equation of state for liquid metals.

Table 1
Optimized parameters for metals

Metal	σ (nm)	ε/k (K)
Lithium	0.2671	3097.0
Sodium	0.3238	2077.9
Potassium	0.4001	1851.4
Rubidium	0.4280	1741.9
Cesium	0.4609	1645.3
Mercury	0.2956	7413.1
Tin	0.2835	2312.8
Lead	0.2952	2398.0
Bismuth	0.2951	1695.5

We have used experimental data for molten potassium to determine the following values for coefficients in Eqs. (8) and (9):

$$a_1 = 1.058393 \quad a_2 = -0.879380$$
$$a_3 = 0.609445 \quad a_4 = -0.314038$$
$$b_1 = 0.798019 \quad b_2 = 0.908086$$
$$b_3 = 0.521304 \quad b_4 = -0.407266.$$

Knowing the values of a_i and b_i, we can predict the equation of state for liquid metals by adjusting ε and σ. The calculated values of ε and σ are listed in Table 1 for metals studied in this work. The best available experimental data for liquid alkali metals [21–26] have been used to test the predictive power of the present equation of state. The experimental data for molten alkali metals cover a broad temperature range from melting point close to the critical point and pressures from saturated vapor pressure to 1000 bar. Also the equation of state has been tested against the experimental data for mercury [26,27], tin, lead, and bismuth [28]. The calculated results for the saturated liquid densities are listed in Table 2 as average absolute deviation. The results

Table 2
The calculation results for the saturated liquid density of metals

Metal	This work			Previous works [12,29]		
	ΔT (K)	NP[a]	AAD[b] (%)	ΔT (K)	NP	AAD (%)
Lithium	453.7–3200	26	1.14	800–2000	13	2.99
Sodium	371–2200	20	1.89	450–1450	11	3.09
Potassium	336.7–2100	19	1.97	336.7–1150	9	3.05
Rubidium	312.5–2000	17	2.22	312.5–1050	8	3.11
Cesium	301.6–1900	17	2.14	301.6–1000	8	3.21
Mercury	234.3–1073.15	29	0.79	243.15–723.15	10	2.98
Tin	623.15–873.15	6	1.80			
Lead	669.15–969.15	7	1.78			
Bismuth	642.15–872.15	6	2.08			
Overall		147	1.62		59	3.06

[a] NP represents the number of data points examined.

[b]
$$AAD = 100/NP \sum_{i=1}^{NP} |\rho_{i,Cal.} - \rho_{i,Exp.}|/\rho_{i,Exp.}.$$

H. Eslami / Journal of Nuclear Materials 336 (2005) 135–139

Table 3
The calculation results for the compressed liquid density of metals

Metal	Δp (bar)	This work			Eslami et al. [13]		
		ΔT (K)	NP	AAD (%)	ΔT (K)	NP	AAD (%)
Lithium	100–1000	500–2000	94	1.20	500–1200	45	2.38
Sodium	100–1000	400–2000	97	1.33	400–1200	48	2.25
Potassium	50–1000	400–1900	122	1.72	400–1200	48	1.96
Rubidium	50–1000	400–2000	112	1.63	400–1000	43	1.88
Cesium	50–1000	400–2000	119	1.81	400–1000	43	2.16
Mercury	0–4000	290.15–427.15	80	2.06			
Tin	1000–2000	722.15–931.15	9	3.46			
Lead	1000–3000	669.15–921.15	12	1.58			
Bismuth	1000–2000	667.15–869.15	7	1.48			
Overall			652	1.64		227	2.13

of the present calculations for the saturated liquid density of alkali metals and mercury are also compared with the previous equations of state by Ghatee and Boushehri [12] and Mehdipour nad Boushehri [29], respectively. The equation of state is also employed to calculate the compressed liquid density of metals over a wide pressure range. The results are reported in Table 3 and are compared with our previous calculations [13]. In order to show how the equation of state passes through the experimental points, deviation plots for the saturated liquid density of lithium, potassium, cesium, and mercury are shown in Fig. 1. Also the deviation plots for the calculated liquid density of liquid potassium, as a typical example, compared with experiment at three isobars are plotted in Fig. 2. Comparison of the tabulated results in Table 2 shows that the present work is more
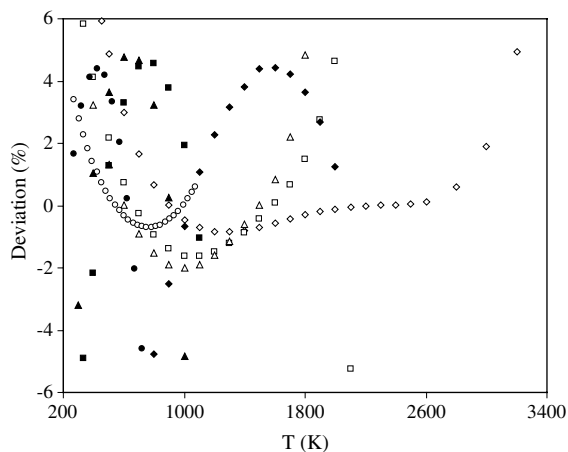

Fig. 1. Deviation plot for the predicted saturated liquid density of Li ($\diamond$), K ($\square$), Cs ($\triangle$), and Hg ($\circ$) compared with experiment. The open markers show the results of the present equation of state and the corresponding filled ones are from the previous equations of state for alkali metals [12] and mercury [29].
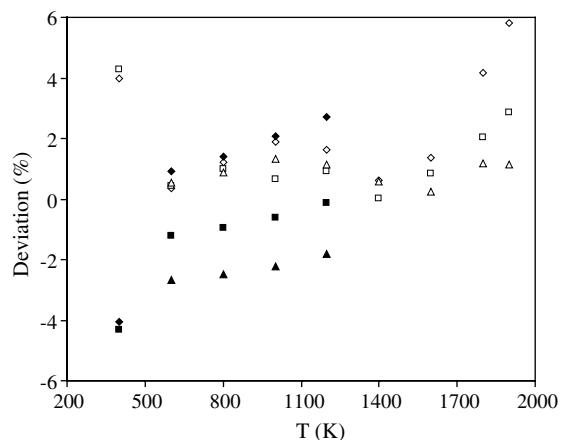

Fig. 2. Deviation plot for the predicted compressed liquid density of Cs at 100 bar ($\diamond$), 600 bar ($\square$), and 1000 bar ($\triangle$) compared with experiment. The open markers show the results of the present equation of state and the corresponding filled ones are from the previous equation of state [13].

accurate and covers a wider temperature range than that of previous works [12,29]. For the present equation of state the results in Fig. 1 shows that 80% of points are located between ±2% of experimental data, while 22.5% of the predicted results from the previous equations of state [12,29] are located in this interval. Also the results of Table 3 and Fig. 2 for compressed liquid metals show that the present equation of state works better than our previous one [13] and its accuracy remains good over an extended temperature range.

This work shows that the equation of state for ordinary fluids can be extended to include liquid metals. Two adjustable parameters, ε and σ, are required for this purpose, instead of three adjustable ones for ordinary fluids. There is no need to know the exact potential energy curve for calculation of the temperature-dependent parameters. Although the electrons in metals interact

with each other and with atomic cores through a long range potential, but due to the nature of bonding in metals the total electronic potential than an electron sees is almost constant from point to point. Therefore it is reasonable to accept that many of the physically observable properties of metallic systems are not so sensitive to the details of the electron–electron and electron-core interactions. For example, due to ns^1 electronic configuration of alkali metals these metals interact via two singlet and triplet type potentials. The results of this work show that even for these metals the present equation of state is applicable as well, i.e., the influence of the two potential types on them is taken into account in an average way in parameters a and b of the equation of state. Moreover, the parameters a and b are not dependent on the details of the potential energy function. Of course, it is worth considering that some of the inherent errors hidden in this method for calculation of a and b can be somewhat compensated by adjusting ε and σ. Although the present equation of state is compared against the experimental data for nine metals, lack of experimental data on other metals prevents us to check its accuracy for the prediction of their pvT properties.

Acknowledgment

References

[1] W. Wang, M.K. Khoshkbarchi, J.H. Vera, Fluid Phase Equil. 115 (1996) 25.
[2] M.K. Khoshkbarchi, J.H. Vera, Fluid Phase Equil. 130 (1997) 189.
[3] M.K. Khoshkbarchi, J.H. Vera, Fluid Phase Equil. 142 (1998) 131.
[4] Y. Song, E.A. Mason, J. Chem. Phys. 91 (1989) 7840.
[5] G. Ihm, Y. Song, E.A. Mason, J. Chem. Phys. 94 (1991) 3839.
[6] Y. Song, J. Chem. Phys. 92 (1990) 2683.
[7] G. Ihm, E.A. Mason, Mol. Phys. 71 (1990) 109.
[8] Y. Song, E.A. Mason, J. Chem. Phys. 93 (1990) 686.
[9] Y. Song, E.A. Mason, Phys. Rev. A 42 (1990) 4743.
[10] Y. Song, E.A. Mason, Phys. Rev. A 42 (1990) 4749.
[11] G. Ihm, Y. Song, E.A. Mason, Mol. Phys. 75 (1992) 897.
[12] M.H. Ghatee, A. Boushehri, Int. J. Thermophys. 16 (1995) 1429.
[13] H. Eslami, S. Sheikh, A. Boushehri, High Temp. High Press. 33 (2001) 725.
[14] Y. Song, S.M. Lambert, J.M. Prausnitz, IEC Res. 33 (1994) 1047.
[15] Y.C. Chiew, Mol. Phys. 70 (1990) 129.
[16] N.F. Carnahan, K.E. Starling, J. Chem. Phys. 51 (1969) 635.
[17] Y. Song, E.A. Mason, Fluid Phase Equil. 75 (1992) 105.
[18] 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.
[19] P.S. Fialho, J.M.N.A. Fareleira, M.L.V. Ramires, C.A. Nieto de Castro, Ber. Bunsenges. Phys. Chem. 97 (1993) 1487.
[20] 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.
[21] N.B. Vargaftik, Y.K. Vinogradov, V.S. Yargin, Handbook of physical properties of liquids and gases: pure substances and mixtures, third Ed., Begell House, New York, 1996.
[22] N.B. Vargaftik, V.A. Alekseev, V.F. Kozhevnikov, Yu.F. Ryzhkov, V.G. Stepanov, Inzh.-Fiz. Zh. 35 (1978) 901.
[23] N.B. Vargaftik, V.F. Kozhevnikov, V.A. Alekseev, Inzh.-Fiz. Zh. 35 (1978) 998.
[24] N.B. Vargaftik, V.F. Kozhevnikov, P.N. Ermilov, High Temp. High. Press. 16 (1984) 233.
[25] N.B. Vargaftik, V.F. Kozhevnikov, V.G. Stepanov, V.A. Alekseev, Yu. F. Ryzhkov, F. Yu in: A. Cezairliyan (Ed.), Proceedings 7th Symposium, Thermophys. Prop., New York, 1977.
[26] N.B. Vargaftik, V.F. Kozhevnikov, P.N. Ermilov, V.A. Alekseev, in: J.V. Sengers (Ed.), Proceedings 8th Symposium Thermophys. Prop., New York, 1982.
[27] G.J.F. Holman, C.A. ten Seldam, J. Phys. Chem. Ref. Data 23 (1994) 807.
[28] A.R. Hansen, C.A. Eckert, J. Chem. Eng. Data 36 (1991) 252.
[29] N. Mehdipour, A. Boushehri, Int. J. Thermophys. 18 (1997) 1329.