

Investigation of Thermodynamic Properties of Heavy Metals from Melting and Critical Point Properties

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ABSTRACT: A statistical mechanical based equation of state has been employed to calculate the liquid density of lead, mercury, bismuth and lead-bismuth and lead-lithium eutectic alloys. The equation is basically that of Song, Mason and Ihm [Ihm G, Song Y, Mason EA. *J. Chem. Phys.* 1991; 94: 3839] which is modified by Ghatee and Boushehri. Three temperature dependent parameters are required to use this equation of state. The second virial coefficient B_2 , an effective van der Waals co-volume, b and a correction factor α . B_2 is predicted from a corresponding states correlation with two scaling parameters, melting point temperature, T_m and liquid density at melting point, ρ_m . Liquid densities are predicted from melting point up to several hundred degrees above the melting point. The results are fairly consistent with experiment. In order to evaluate the correlation equation, Tao and Mason equation of state is applied to the above cited liquid metals and liquid density results are compared to the present equation. Obviously, the first equation acts better.

KEY WORDS: Heavy metals, Equation of state, Surface tension, Density.

INTRODUCTION

Heavy Liquid Metals (HLM), such as mercury (Hg), lead (Pb), bismuth (Bi) and lead-bismuth eutectic (Pb-Bi), have been studied in several countries as potential materials for spallation neutron sources driven by proton or electron accelerator because of a high neutron yield per incident high energy particle [1]. The lead-lithium eutectic is regarded as one of the basic tritium breeding materials of the blanket of ITER fusion reactor [2].

However, experimental data on HLM properties in the temperature range of interest are rare. Therefore and because of the difficulties of experimental measurement, the prediction of these properties with the help of an adequate Equation Of State (EOS) developed on the basis of fundamental thermodynamics

and limited empirical data can be a valuable alternate. Once EOS is known for a fluid, one can determine its various thermodynamic properties at equilibrium.

Here the starting point is the ISM EOS, which was proposed primarily by Song & Mason [3] and extended later by Ihm *et al.* [4]. This EOS includes three parameters in the final form, $B_2(T)$, the second virial coefficient, $b(T)$, the effective van der Waals co-volume, and $\alpha(T)$, a scaling factor. All of these parameters can be calculated by integration, if the intermolecular potential is accurately known. In the absence of such information, the second virial coefficient data suffice to predict the entire (p- ρ -T) surface of fluids since

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the other two coefficients can be derived from B_2 . For the metals, which are of interest in this work, neither exact intermolecular potential energies nor experimental second virial coefficients exist in the literature. At this point, the most useful method is to predict the second virial coefficient, B_2 , and consequently the two other parameters, b and α with the help of the principle of corresponding states which is a useful guide for estimating the behavior of dense gases and liquids. This principle is usually applicable by the reduction of the macroscopic (critical point) or molecular (potential energy) parameters.

Many investigators have designated methods for predicting the second virial coefficients, and hence the EOS, from different scaling factors such as critical constants [5], the heat of vaporization and liquid density at the triple point [6] and boiling point [7], surface tension and the liquid density at the freezing point [8] and boiling point [9] and the boiling point parameters [10].

Here, the second virials at different temperatures are calculated using two different sets of corresponding states correlations. First, those correlated by *Ghatee & Boushehri* (GB)[7] and the second set, by *Tao & Mason* (TM) [4]. It has been shown that GB correlation leads to an analytical EOS that can predict the liquid densities of lead, lead-bismuth and lead-lithium eutectic alloys consistently up to hundreds of Kelvin above the melting point. The TM procedure didn't show any good results.

THEORITICAL SECTION

The starting point in derivation of the ISM equation of state is the following equation that relates the pressure, p , to the pair distribution function $g(r)$ [11]

$$\frac{p}{\rho RT} = 1 - \frac{2\pi}{3} \frac{\rho}{RT} \int_0^{\infty} \frac{du}{dr} g(r) r^3 dr \quad (1)$$

in which $u(r)$ is the pair potential as a function of distance r and R is the universal gas constant. Many body effects are incorporated through the distribution function, $g(r)$.

The Rearrangement of this equation to a form with explicit second virial coefficient, dividing the potential function similar to *Weeks, Chandler & Anderson* [12] and substituting $g(r)$ by the *Carnahan Starling* formula [13] in addition to some approximations leads to the complete form of the ISM equation of state.

$$\frac{p}{\rho RT} = 1 - \frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \quad (2)$$

Where λ is the only adjustable parameter of this equation. B_2 is the second virial coefficient and α and b which can be derived from B_2 are the repulsive contribution to the second virial coefficient and the van der Waals co-volume, respectively. If the values of these three parameters are known, the free parameter λ is best found from experimental p - ρ - T data, but a few reliable liquid densities may be sufficient for the purpose. Then the density at each temperature and pressure can be calculated by means of the cubic EOS.

It is clear that $B_2(T)$ plays a central role in this equation of state. Not only it is used directly, But it is the source of the Boyle constants used to find $\alpha(T)$ and $b(T)$ [3]. Since for metals there is no experimental second virial coefficient data, the corresponding states correlations are utilized to calculate the three temperature dependent parameters.

Corresponding States Correlation

Ghatee & Boushehri [8], Proposed the following equation based on the surface tension and liquid density at melting point for normal fluids:

$$B_2(T)\rho_m = 0.0804 - 2.1288T^{*-1} - 8.5597T^{*-2} + 7.4294T^{*-3} - 3.3494T^{*-4} \quad (3)$$

with

$$T^* = \left[T T^{0.5} / T_{ref} T_m^{0.5} \right]^{3/4} \quad (4)$$

and

$$T_{ref} = \gamma_m \rho_m^{-2/3} N^{1/3} / R \quad (5)$$

T_m is the melting point temperature and ρ_m (mol/L) and γ_m (N/m) are the density and the surface tension of fluid at T_m . N is Avogadro's number.

$$\alpha\rho_m = a_1 \left[\exp(-c_1 T^*) \right] + a_2 \left[1 - \exp(c_2 / T^{*1/4}) \right] \quad (6)$$

$$b\rho_m = a_1 (1 - c_1 T^*) \left[\exp(-c_1 T^*) \right] + \quad (7)$$

$$a_2 \left[1 - \left(1 + \left(0.25 c_2 / T^{*1/4} \right) \right) \exp(-c_2 / T^{*1/4}) \right]$$

Table 1: Characteristic melting point parameters for HLM.

HLM	GMW (g/mol)	T _m (K)	γ _m (N/m)	ρ _m (mol/L)	λ
Hg	200.59	234.32 [16]	0.49 [16]	68.25 [16]	0.370
Pb-Bi	208.19	398.15 [15]	0.41 [15]	50.57 [15]	0.449
Pb	207.20	600.6 [14]	0.45 [14]	51.39 [14]	0.449
Pb-Li	173.16	508.1 [15]	0.48 [15]	57.26 [15]	0.477

Table 2: Density calculation results from the equation of state compared to the experimental data using Ghatte and Boushehri correlations.

substance	No. of the points	Temperature range, ΔT(K)	AAD ^a (%)	Deviation percent Range	Ref.
Hg	11	224.65-723.15	3.48	-6.19-6.34	[16]
Pb-Bi	7	673.15-1273.15	1.86	-3.97-3.24	[1,17]
Pb	6	601.15-1073.15	2.32	-1.26-2.48	[14]
Pb-Li	9	600-1000	2.53	-3.46-2.98	[2]

$$^a \text{AAD} = 100 / \text{NP} \sum_{i=1}^{\text{NP}} |p_{i,\text{Cal.}} - p_{i,\text{exp.}}| / p_{i,\text{exp.}}$$

where

$$a_1 = -0.01054, \quad c_1 = 0.7613$$

$$a_2 = 2.9387, \quad c_2 = 1.3227$$

On the other hand, Tao & Mason furnished the following expressions:

$$\left(\frac{p_c}{RT_c} \right) B_2 = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (8)$$

where $T_r = \frac{T}{T_c}$ and the group $\left(\frac{RT_c}{P_c} \right)$ serves as

a critical volume. $f^{(0)}(T_r)$ and $f^{(1)}(T_r)$ read as:

$$f^{(0)}(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^3} \quad (9)$$

and

$$f^{(1)}(T_r) = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^3} \quad (10)$$

$$\alpha / v_B = a'_1 \left[\exp(-c'_1 / (T/T_B)) \right] + \quad (11)$$

$$a'_2 \left[1 - \exp\left(c'_2 / (T/T_B)^{1/4} \right) \right]$$

and

$$b / v_B = a'_1 (1 - c'_1 (T/T_B)) \left[\exp(-c'_1 (T/T_B)) \right] + \quad (12)$$

$$a'_2 \left[1 - \left(1 + \left(0.25 c'_2 / (T/T_B)^{1/4} \right) \right) \exp\left(-c'_2 / (T/T_B)^{1/4} \right) \right]$$

where, T_B and v_B are the Boyle temperature and volume and are represented as:

$$\frac{T_B}{T_c} = 2.6455 - 1.1941\omega \quad (13)$$

and

$$v_B \left(\frac{p_c}{RT_c} \right) = 0.1646 + 0.1014\omega \quad (14)$$

The values of a'₁, a'₂, c'₁ and c'₂ are -0.0648, 1.8067, 2.6038 and 0.9726, respectively.

RESULTS AND DISCUSSION

The melting point parameters of systems were found in refs. [14-17]. B₂(T), α(T) and b(T) are calculated using equations (3-6). The scaling constants, ρ_m, γ_m and T_m for the systems are collected in Table 1. Also λ is reported in this table. It is calculated by fitting Eq. (2) to experimental data. The numerical values for λ are also given in Table 1. Finally the densities are predicted through Eq. (2) as a cubic equation of state. In general, agreement with experiment is good. The deviation percents are usually within 4%. Average absolute deviations are reported in Table 2. Although the results listed in Table 2 show the degree of consistency between this model and experimental data, the results are also shown in Fig. 1,

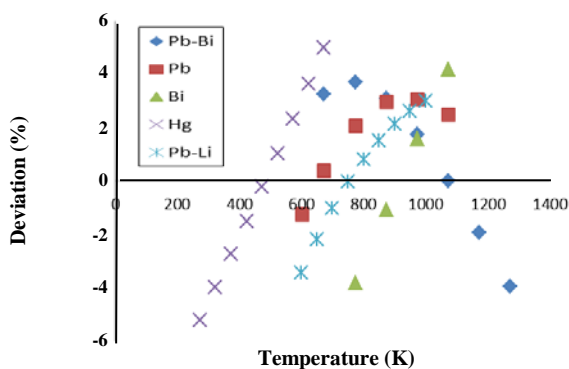


Fig. 1: Deviation patterns, the GB correlation.

on which any deviation pattern is more obvious. Hg and Bi showed some good consistencies in density data but density data against temperature did not give a good trend. Therefore, their thermodynamic properties cannot be derived from this equation. This is shown in Fig. 2.

Since the ISM equation of state is analytical and based on a mean-field approximation, it does not work accurately in the non-analytical two-phase and critical regions as it is clearly mentioned by *Ihm et al.* [4]. Also the Maxwell construction does not make satisfactory results. The results are the poorest at low temperatures where the van der Waals loops are larger. Therefore, it is impossible to accurately calculate the vapor-pressure curve via the present equation of state. Some mathematically similar equations (such as Redlich-Wong and Peng Robinson) are usually empirically adjusted to give good vapor pressures via the Maxwell construction. However this occurs at the expense of the liquid branches of the isotherms, so that poor values of liquid densities are predicted[4].

The fact that the second virial coefficients of metals obey the law of corresponding states may be unexpected. However, Eqs. (3)–(6) for $B_2(T)$, $\alpha(T)$ and $b(T)$ based on a corresponding-states correlation with the surface tension and the liquid density at melting point as scaling constants can produce relatively accurate results. Of course, some of the errors in this procedure can be compensated by adjusting the parameter λ by fitting to experimental P – ρ – T data.

Here is indicated that only two characteristic constants, the liquid density and the surface tension

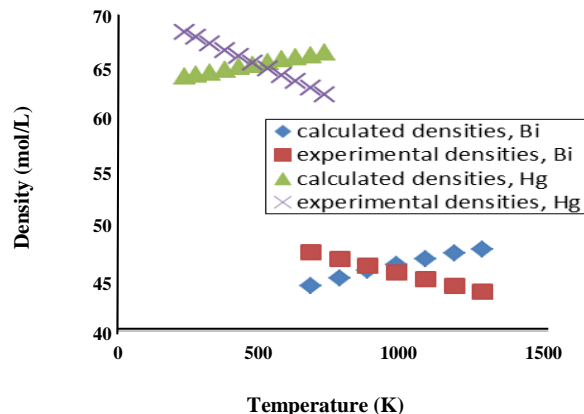


Fig. 2: Density against temperature for Bi and Hg, the GB correlation.

at the melting point, are sufficient to predict the liquid density of Pb, Pb- Bi and Pb- Li eutectic alloys, without knowing the whole potential energy curve or the experimental second virial coefficients of these metals.

Secondly TM correlations are used to predict density data for Pb, Bi, Pb-Bi eutectics. The critical properties were adopted from [2, 17-22]. Data are collected in Table 3. Different data in literature are tested but just one of them is reported for each substance. λ is calculated from ω which is derived by fitting to the experiment. Critical properties, λ 's and average absolute deviation percents (AAD%) are reported in Table 3. No acceptable predictions resulted. Densities against temperature for Pb and Pb-Bi are illustrated in Fig. 3. It is obvious that this job is impossible or weakly possible through critical data. It may be due to the non unique and non accurate critical data in literature. Also some other works show that GB corresponding states correlation is stronger than TM. This is able to reproduce the p – ρ – T surface for many different groups of material such as normal fluids[8], polymers [23] and many metals[24-26]. TM equation is used by *Yousefi & Kaveh* for refractory metals[27] and some other liquids but they have fitted all the coefficients of the correlation for each liquid. Obviously this is not a helpful corresponding states law.

CONCLUSIONS

An equation of state is developed which correlates the volumetric properties for Pb, Pb- Bi and Pb-Li eutectic alloys. As it is obvious, the ISM EOS with GB correlations can be applied usefully to predict the p – ρ – T

Table 3: Characteristic critical point parameters for HLM.

HLM	T _c (K)	P _c (MPa)	AAD%	λ
Pb [1,18]	4967	103.0	3.65	0.146
Bi [1,18,19]	4420	139	4.54	0.356
Hg [1,19]	1762	157.8	43.48	0.415
Pb-Bi [1,20,21,22]	4890	87.8	4.13	0.133

behavior of these metallic liquids. Due to the compensating effects of λ , the extrapolation of normal fluids' corresponding states correlation [7] to the metallic region does not put an important effect on the final results.

Knowledge of density and surface tension of each substance in conjunction with an adjustable parameter is enough to utilize the equation. The equation does not reproduce the vapor pressure due to its analytic nature and mean field approximations.

Also it is shown that this correlation is inappropriate through critical data and *Tao-Mason* correlations.

Nomenclature

ω	Acentric factor (here is adjusted), unit less
λ	Adjustable parameter, unit less
T _B	Boyle temperature, K
a_1, a_2, c_1 and c_2	Coefficients of correlation GB, unit less
a'_1, a'_2, c'_1 and c'_2	Coefficients of correlation TM, unit less
T _c	Critical temperature, K
p _c	Critical pressure, pa
ρ_m	Density at melting point, mol/m ³
r	Distance, m
ρ	Density
g(r)	Distribution function
b(T)	Effective van der Waals co-volume m ³ /mol
T _m	Melting point temperature, K
u(r)	Pair potential, J/mol
p	Pressure, pa
T*	Reduced temperature (GB), unit less
T _r	Reduced temperature (TM), unit less
B ₂ (T)	Second virial coefficient, m ³ /mol
$\alpha(T)$	Scaling factor, m ³ /mol
T	Temperature, K
R	Universal gas constant, J/(mol.K)

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