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Song and mason equation of state for metals: prediction from boiling point constants

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ABSTRACT

A statistical-mechanical analytical equation of state has been employed successfully to alkali metals, alkaline earth metals, aluminum, bismuth and lead. There exist three temperature dependent parameters in the equation of state; the second virial coefficient, an effective molecular volume, and a scaling factor for the average contact pair distribution function of hard convex bodies. The temperature-dependant parameters have been calculated using corresponding-states correlations based on normal boiling point parameters as scaling constants. It is shown that knowledge of just normal boiling temperature and the liquid density at the normal boiling point are sufficient to predict the equation of state of alkali metals, alkaline earth metals, aluminum, bismuth and lead. The theory has considerable predictive power, since it permits the construction of the *PVT* surface from the normal boiling temperature and the liquid density at the normal boiling point. The average absolute deviation for the calculated densities of metals is 1.14 %.

KEYWORDS

Alkaline earth metals;
Alkali metals;
Equation of state;
Liquid density;
Normal boiling point;
Statistical mechanics.

INTRODUCTION

Liquid metals show various characteristics that are invaluable in industrial applications. Features such as high boiling temperatures, extended liquid range, low vapor pressure, high thermal conductivity, and high heat of vaporization are have made them applicable in various operations such as metallurgy, glass forming, casting, welding, and crystal growth. These properties have given them also a great significance as coolants in nuclear power plants. Amongst the liquid metals, liquid alkali metals and liquid alkaline earth metals have been used widely for this purpose. Therefore a precise knowledge of their thermodynamic properties seems to be extremely helpful. Although, estimation of the density of liquid metals is necessary in the process of computer simulation, in the calculation of other thermodynamic properties, and in extracting quantitative structural information from diffraction spectra[1]. Unfortunately, for metals, difficult experimental conditions such as low vapor pressures and high temperatures restrict the experimental measurements.

Molecular simulation methods[2,3] can used to predict thermophysical properties of metals. Despite the precision, molecular simulation methods are computationally expensive and need accurate potential energy function for this purpose.

Accurate knowledge of the mechanical behavior of fluids using equations of state is always worth in thermophysical studies. Among the proposed equations of state by different investigators, the analytical equations that have been established on a theoretical basis are a few. Although many attempts have been made to make progress in this field, the lack of a proper universal potential energy function still impresses many unsolved problems.

The conventional methods for the prediction of volumetric properties of fluids are based on the equation of state (EOS) and corresponding-states correlation methods[4,11]. If, in the first place, accurate input data are available, the applicability of an EOS to a given system is reliable. In practice, the input data may not be available or it may not be possible to measure these data accurately for a given system. However, there are some equations of state which are precise enough over a wide range of temperatures and just need some easily available input parameters[12–14].

In this work, an analytical equation of state based on statistical mechanical perturbation theory proposed by Song and Mason[15] is of special interest. This equation with correlation procedure by Eslami[16] can be used with even less input information for alkali metals (Li through Cs), liquid alkaline earth metals (Mg through Ba), aluminum, bismuth and lead over a wide range of temperatures and pressures. In particular, knowledge of only two constant, the normal boiling temperature and the liquid density at the normal boiling point as scaling parameters is sufficient to predict the *PVT* properties of these metals over a wide range of temperatures and pressures.

THEORETICAL EQUATION OF STATE

Song and Mason[15] proposed an analytical equation of state for convex-molecular fluids based on statistical-mechanical perturbation theory. The equation of state is of the form:

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + \alpha(T)\rho[G(\eta) - 1] \quad (1)$$

where P is the pressure, ρ is the molar (number) density, $B_2(T)$ is the second virial coefficient, $\alpha(T)$ is the contribution of the repulsive forces to the second virial coefficient, $G(\eta)$ is the average pair distribution function at contact for equivalent hard convex bodies, η is the packing fraction, and kT is the thermal energy per one molecule. Song and Mason[15] adopted the following form for $G(\eta)$, which is shown to be accurate for hard convex bodies[15,17].

$$G(\eta) = \frac{1 - \gamma_1\eta + \gamma_2\eta^2}{(1-\eta)^3} \quad (2)$$

where γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients. In practice γ_1 and γ_2 can be approximated in terms of a single nonsphericity parameter γ, equal to unity for hard spheres. The parameters γ_1 and γ_2 have been defined in terms of γ as[15]:

$$\gamma_1 = 3 - \frac{1 + 6\gamma + 3\gamma^2}{1 + 3\gamma} \quad (3)$$

and

$$\gamma_2 = 3 - \frac{2 + 2.64\gamma + 7\gamma^2}{1 + 3\gamma} \quad (4)$$

The packing fraction, η, is given by

$$\eta = \frac{b(T)\rho}{1 + 3\gamma} \quad (5)$$

where b is the van der Waals covolume and can be defined in terms of α as[15]:

$$\mathrm{b(T)} = \alpha(\mathrm{T}) + \mathrm{T}\frac{\mathrm{d}\alpha(\mathrm{T})}{\mathrm{dT}} \quad (6)$$

Once the intermolecular potential energy function is known, the temperature-dependent parameters $B_2(T)$, $\alpha(T)$, and $b(T)$ can be found by three integrations, and γ is the best found by fitting available *P-V-T* data[15].

Several procedures can be employed to determine the temperature-dependent parameters. Generally, one may perform the integral equations derived by Song and Mason[18] which require the pair potential energy function of physical systems. Since the pair potential energy is seldom accurately known for most physical systems of interest, we have to employ another alternative method to calculate the temperature-dependent parameters. In these circumstances, fortunately, there are some correlation procedures have been developed in the literature via surface tension data[19-21], boiling point constants[16,22] and critical point constants[23,24]. In this work, we aim to use the correlation based on the normal boiling point parameters, liquid density at the normal boiling point, ρ_{nb}, and normal boiling temperature, T_{nb}, as two scaling parameters[16]:

$$\mathbf{B}_2^*(\mathbf{T}) = 1.033 - 3.0069\mathbf{T}^* - 10.588\mathbf{T}^{*2} + 13.096\mathbf{T}^{*3} - 9.8968\mathbf{T}^{*4} \quad (7)$$

With

$$\mathbf{T}^* = \frac{\mathbf{T}}{\mathbf{T}_{nb}} \quad (8)$$

and

$$\mathbf{B}_2^*(\mathbf{T}) = \mathbf{B}_2(\mathbf{T})\rho_{nb} \quad (9)$$

where, ρ_{nb} *and* T_{nb} represent the liquid density at the normal boiling point and the normal boiling temperature, respectively.

Song and Mason[18] indicated that the reduced temperature-dependant parameters, $\alpha(T)$, and $b(T)$, are universal functions of the reduced temperature when reduced in terms of the Boyle parameters. Also they indicated that $\alpha(T)$, and $b(T)$ are relatively insensitive to the detail of the potential energy function[18]. Therefore, they proposed two empirical formulas for reduced $\alpha(T)$, and $b(T)$ in terms of the reduced temperature.

We utilized the same empirical formulas proposed by Song and Mason[25] and rescaled the coefficients of the formulas to consider the effect of changing the scaling constants from the Boyle parameters to the temperature and the liquid density at the normal boiling points, i.e.

$$\alpha(\mathbf{T})\rho_{nb} = \mathbf{a}_1 \exp\left(-\mathbf{a}_3\mathbf{T}^*\right) + \mathbf{a}_2\left[1 - \exp\left(-\mathbf{a}_4\mathbf{T}^{*1/4}\right)\right] \quad (10)$$

$$\mathbf{b}(\mathbf{T})\rho_{nb} = \mathbf{a}_1\left(1 - \mathbf{a}_3\mathbf{T}^*\right)\exp\left(-\mathbf{a}_3\mathbf{T}^*\right) \cdot$$

$$) + \mathbf{a}_2\left\{1 - \left[1 + 1/4\mathbf{a}_4\left(\mathbf{T}^*\right)^{-1/4}\right] \exp\left[-\mathbf{a}_4\left(\mathbf{T}^*\right)^{-1/4}\right]\right\} \quad (11)$$

where a_1,a_2, a_3, a_4 are 2.080017, 2.204481, 0.509251, 0.894258 respectively. Therefore known value of the boiling point parameters make permit to determine the temperature dependent parameters of the equation of state. The remaining problem is to find γ from *PVT* data. This adjustable parameter is determined by fitting the high density experimental *PVT* data. Once the value of the constant γ is determined, the entire volumetric behavior is established. The values of γ for each fluid are given in TABLE 1.

In this work we apply the equation of state, "equation (1)", with the temperature dependent parameters determined using the corresponding-states correlation based on temperature and liquid density at the normal boiling point as scaling constants, "equations (7), (10) and (11)", to determine *PVT* properties of alkali metals, alkaline earth metals, aluminum, bismuth and lead over a wide range of temperatures and pressures.

RESULTS AND DISCUSSION

In this work, Song and Mason EOS was applied to some pure metals containing alkali metals, alkaline earth metals, aluminum, bismuth and lead. The normal boiling point parameters of metals are used as input data, to determine temperature-dependent parameters and the adjustable parameter was calculated by knowing experimental *PVT* data. Values obtained for γ as well as boiling point parameters for metals are listed in

TABLE 1 : Parameters used for metals

Substance	T_{nb}(K)	ρ_{nb} (mol m^{-3})	γ
Li	1615	57567.7	1.011
Na	1151.2	32334.3	0.994
K	1032.3	16969.3	0.998
Rb	959	13733.1	1.003
Cs	943	11067.5	0.997
Mg	1366.4	60480.0	0.977
Ca	1768.4	30620.0	0.990
Sr	1659.3	24780.0	0.977
Ba	2120	21920.0	0.923
Al	2330	73420	0.999
Bi	1723	48090	0.950
Pb	2017	43220	0.967

TABLE 1. Actually the purpose of this work is to show how this equation of state can be applied with even less input information for metals. The obtained densities compared comprehensively with a large number of experimental liquid densities over a wide range of temperatures and pressures, and the results are given in TABLE 2 along with the AAD (average absolute deviation). All of the results in this table are compared with experimental data[26,27]. As TABLE 2 shows; the agreement between the calculated and experimental data of these metals is very good. In general, the obtained mean of the deviations for all alkali metal and alkaline earth metals was found to be of the order of 0.63% and 2.07%, respectively.

It is a matter of considerable practical importance to compare this EOS with other equations of state. In this respect, we have compared our results for alkali metals with those obtained using Mehdipour et al.[28] and for alkaline earth metals with Eslami et al.[29]. The results of the calculations for all alkali metals and alkaline earth metals are gathered in TABLE 2. It is obvious that, our results are in favor of the preference of the Song and Mason EOS over ISM equation of state. The overall average absolute deviation that calculated by Mohdipour et al.[28] and Eslami et al.[29] are 1.16% and 2.36%, respectively. The values of calculated densities for alkali metals and alkaline earth metals and comparison of deviation of experimental data[26,27] with those obtained using Mehdipour et al.[28] and Eslami et al.[29] for each data points are presented as TABLES SI1

TABLE 2 : The calculated results for the liquid density of metals compared with experimental data[26,27] and the results of the ISM equation of state[28,29]

Substance	Range of temperature(K)	Range of pressure(bar)	AAD% [a]	
			Present work	Ref.[19,24]
Li	850-2000	3.72×10^{-5}-8.64	0.67	1.8
Na	550-1450	8.88×10^{-6}-3.38	0.45	1.5
K	450-1400	3.21×10^{-6}-12.44	0.70	1.0
Rb	400-1300	1.69×10^{-6}-11.43	0.72	0.99
Cs	400-1200	3.83×10^{-6}-6.79	0.62	0.49
Mg	923-1900	3.59×10^{-3}-21.77	2.4	3.14
Ca	1114-2000	2.06×10^{-3}-3.32	0.86	1.54
Sr	1041-1900	2.5×10^{-3}-2.38	2.94	3.18
Ba	1000-2000	7.06×10^{-5}-0.62	2.08	1.59

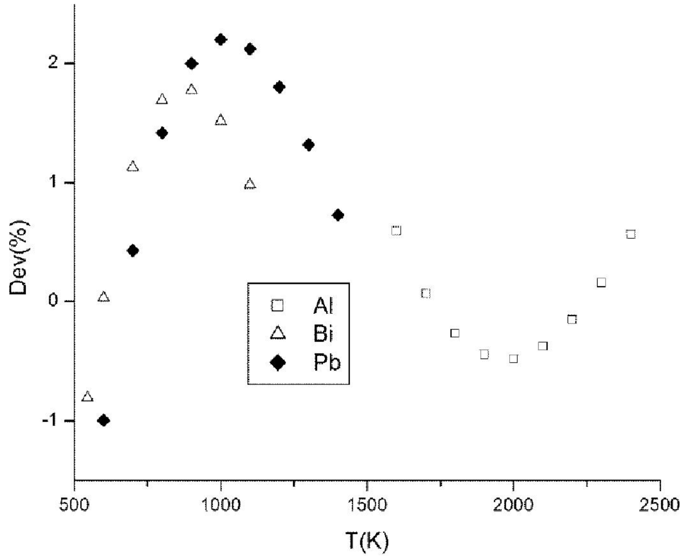

Figure 1 : Deviation plot from experimental data[30,31] for calculated liquid densities by this equation of state as a function of temperature for Al, Bi, Pb

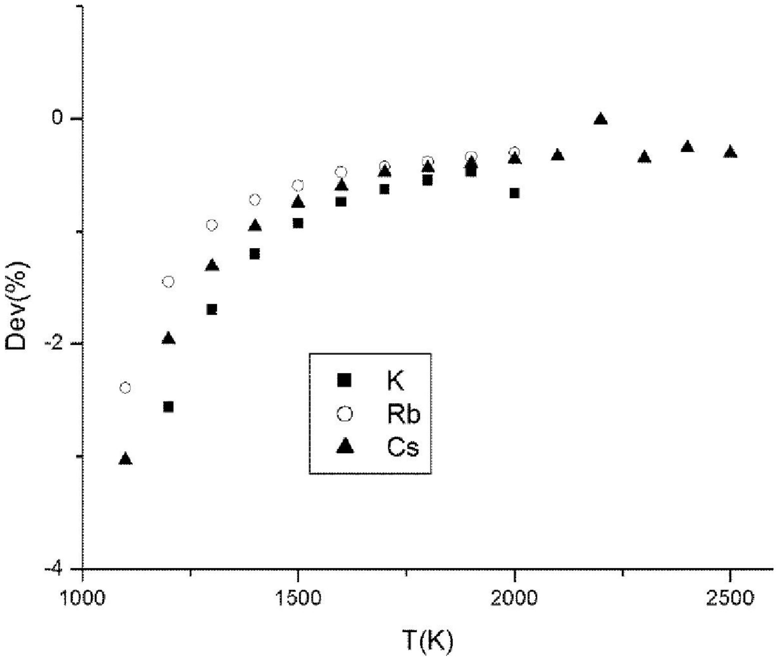

Figure 2 : Deviation plot from experimental data[26] for calculated vapor densities at P=1bar by this equation of state as a function of temperature for K, Rb, Cs

and SI2of the supplementary information.

Also, we performed the calculation of molar volume of Al, Bi, Pb, at different temperature and pressure and the results are compared with experimental data[30,31] in Figure 1. As Figure 1 shows, the calculated results agreed truly with the experiment.

Although, this equation of state is applied for vapor density K, Rb and Cs at different temperature and P=1bar and the results are compared with experimental data[26] in Figure 2. As Figure 2 shows, the results are satisfactory.

Comparison of our calculated densities in TABLES 2, Figures 1 and 2 with experiment[26,27] show that the present equation of state can well reproduce the density of alkali metals, alkaline earth metals, aluminum, bismuth and lead over a wide range of temperatures and pressures. We showed that for calculating the second virial coefficients, $\alpha(T)$ and $b(T)$, there is no need to know an accurate potential energy function or to know the values of the critical constants. It can be calculated using simple scaling constants, which are readily available.

CONCLUSIONS

In the present work, we have successfully applied the Song and Mason EOS to metals. The calculated results agreed well with the experiment, the obtained mean of the deviations for all alkali metals and alkaline earth metals were found to be of the order of 0.63% and 2.07% respectively. The present equation of state was further assessed through comparisons with Mehdipour et al.[28] and Eslami et al.[29]. Also, we performed the calculation of density of Al, Bi, Pb using Song and Mason EOS. The calculated results of aforementioned metals are compared with experimental data[30,31]. The overall average absolute deviation of this EOS is 0.98%. This equation was applied to calculate vapor density of potassium, rubidium and cesium. The obtained mean of deviation for vapor densities were 0.87%.

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Supplementary Information

Supplementary information associated with this article can be found, in the online version, at doi:.

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