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Modeling the volumetric properties of metals from heat of vaporization

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ABSTRACT

We have applied the Song and Mason equation of state [Y. Song, E.A. Mason, Phys. Rev. A 42 (1990) 4743–4748] with a simple modification for alkali metals, alkaline earth metals, aluminum, bismuth, lead, copper and mercury. The present equation of state consists of four temperature dependent parameters. These parameters have been calculated as function of reduced temperature with the use of the law of corresponding states based on latent heat of vaporization and the liquid density at the normal boiling point. The predicted densities were compared with those obtained from the experiment. From 396 data points examined for the aforementioned metals, the total average absolute deviation was found to be 0.72%. Moreover, we indicate that the Zeno line regularity can well be predicted by the proposed model for metals.

1. Introduction

Metals, both in liquid and vapor states, have complex structures. They widely used in modern science and technology, including nuclear energetic, emission electronics, new power-intensive chemical current sources, medicine and act as coolant in nuclear power plants [1,2]. They could be also more effectively used in extraction metallurgy of precious metals from their ores and wastes [2]. These applications need the knowledge of high temperature properties of these metals, because these metals are heated to high-temperatures in these applications [3]. Therefore a precise knowledge of their thermodynamic properties seems to be extremely helpful.

In these circumstances, there is a growing need for an accurate theoretical model to predict the thermodynamic properties of liquid metals. Prediction of the properties of the liquid phase using statistical mechanical equation of state (EOS) and corresponding states law are conventional methods, which is widely used in the case of pure fluids and fluid mixtures. Most of the existing statistical mechanical equations of state (EOSs) are not analytical in nature and considerable numerical calculations are needed to obtain thermodynamic properties. Recently, an analytical EOS based on statistical mechanical perturbation theory has been proposed by Song and Mason [4] for normal fluids. The maximum information needed to apply this equation is the intermolecular potential plus a characteristic constant for each fluid. However, the exact potential energy curve is unknown, except for very simple fluids. In the absence of the intermolecular potential data, the second virial coefficient as function of temperature plus one adjustable constant, characteristic of each substance, are sufficient. If the second virial coefficient is not known experimentally, there are several correlation from corresponding states law by which the second virial coefficient can be calculated as a function of temperature with reasonable accuracy. Boushehri and Mason [5] developed a method for predicting the second virial coefficient, and hence the EOS, from the heat of vaporization as the energy parameter for reducing temperature and the liquid density at the triple point [5] or the normal boiling point [6] as the size parameter for reducing second virial coefficient.

In this regard, we develop an analytical EOS which has been firstly proposed by Song and Mason [7] with a simple modification of alkali metals, alkaline earth metals, aluminum, bismuth, lead, copper and mercury over a wide range of temperatures and pressures. Then, the efficiency of present EOS is compared with experimental data and other EOSs. Moreover, we indicate that the Zeno line regularity can well be predicted by the proposed model for metals.

2. Theoretical equation of state

Song and Mason [7] proposed an analytical EOS for convex molecular fluids based on statistical-mechanical perturbation theory. The Song and Mason (SM) EOS 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 [7] adopted the following form for $G(\eta)$, which is shown to be

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Table 1
Parameters used for metals.

Substance	ΔH_{vap} (J mol^{-1})	ρ_{nb} (mol m^{-3})	b_1	b_2	b_3
Li	151,123.6	57,567.7	0.466	−1.009	18.037
Na	100,857.1	32,334.3	0.450	−1.074	23.465
K	82,392.6	16,969.3	0.479	−1.862	32.763
Rb	74,134.3	13,733.1	0.490	−2.085	35.340
Cs	70,808.7	11,067.5	0.494	−1.452	30.979
Mg	128,050.0	60,480.0	0.469	−3.060	40.772
Ca	151,890.0	30,620.0	0.390	0.283	16.384
Sr	133,920.0	24,780.0	0.608	−6.516	64.526
Ba	142,450.0	21,920.0	0.422	−2.052	41.999
Al	222,224.9	73,420.0	0.414	0.046	13.405
Bi	184,928.3	40,980.0	0.414	−2.331	38.468
Pb	181,187.0	43,220.0	0.422	−1.98	38.810
Cu	300,572.7	124,320.0	0.395	−3.189	32.404
Hg	60,055.0	63,495.7	1.204	−14.383	81.694

accurate for hard convex bodies [7,8]:

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

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 [7]

$$\gamma_1 = 3-\frac{1+6\gamma+3\gamma^2}{1+3\gamma} \tag{3}$$

and

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

The packing fraction, η, is given by

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

where b is the van der Waals covolume and can be defined in terms of α as [7]

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

In the SM EOS, $B_2(T)$ along with the parameters $\alpha(T)$ and $b(T)$ must be known and their values can be computed from a well-known accurate intermolecular potential. In principle, all three can be computed if an accurate intermolecular potential is known. But accurate potential energy functions for real fluid to calculate B_2(T), $\alpha(T)$ and $b(T)$ are scarce. Therefore, it seems reasonable to find other methods to evaluate these parameters. The most generally useful method to predict of the volumetric properties of fluids, such as the second virial coefficient, is the use of the corresponding states law, which came originally from van der Waals in his well-known EOS. In these methods, we need two scaling constants, one to reduce the second virial coefficient and one to reduce the temperature.

In the conventional law of corresponding states, the critical temperature and the critical volume are used for this purpose, but the critical parameters of metals are either scarce or not measured accurately due to the experimental difficulties at the critical point. To solve this problem, recently several correlation procedures have been developed in the literature via surface tension data [9–12], boiling point constants [13,14], critical point constants [15–17] and heat of vaporization [6]. In this work, we aim to use the correlation based on the heat of vaporization, ΔH_{vap}, and liquid density at the normal boiling point, ρ_{nb}, as two scaling parameters [6]:

$$B_2(T)\rho_{nb} = 0.1-0.054\left(\frac{\Delta H_{vap}}{RT}\right)^2 + 0.00028\left(\frac{\Delta H_{vap}}{RT}\right)^4 \tag{7}$$

where, ΔH_{vap} and ρ_{nb} represent the heat of vaporization and liquid density at the normal boiling point, respectively. The expressions for $\alpha(T)$ and b(T) are [6]:

$$\alpha(T)\rho_{nb} = a_1\left[\exp\left(-a_3\frac{RT}{\Delta H_{vap}}\right) + a_2\left\{1-\exp\left[-a_4\left(\frac{RT}{\Delta H_{vap}}\right)^{-1/4}\right]\right\}\right. \tag{8}$$

$$b(T)\rho_{nb} = a_1\left(1-a_3\frac{RT}{\Delta H_{vap}}\right)\exp\left(-a_3\frac{RT}{\Delta H_{vap}}\right) + a_2\left\{1-\left[1+0.25a_4\left(\frac{RT}{\Delta H_{vap}}\right)^{-1/4}\right]\exp\left[-a_4\left(\frac{RT}{\Delta H_{vap}}\right)^{-1/4}\right]\right\} \tag{9}$$

where a_1,a_2, a_3 and a_4 are −0.11622, 2.22572, 6.58566 and 0.71472, respectively. The heat of vaporization, ΔH_{vap}, and liquid density at the normal boiling point, ρ_{nb}, as initial input data for evaluating $\alpha(T)$, b (T) and $B_2(T)$ have been reported in Table 1. Heat of vaporization at normal boiling temperature was calculated using the Clausius-Clapeyron equation.

The remaining problem now is to find γ. In this respect, the experimental *PVT* data for metals have been taken for this purpose. When determining the free parameter, γ, we observed that this parameter is temperature dependent. Then, the parameter of γ for metals was adjusted by nonlinear regression method as follow:

$$\gamma(T) = b_1 + b_2\left(\frac{RT}{\Delta H_{vap}}\right) + b_3\left(\frac{RT}{\Delta H_{vap}}\right)^2 \tag{10}$$

The coefficients b_1 to b_3 have been reported in Table 1. Generally, a simple procedure has been developed to improve the predictive power of SM EOS for alkali metals, alkaline earth metals, aluminum, bismuth, lead, copper and mercury based on their heat of vaporization and liquid density at the normal boiling point property.

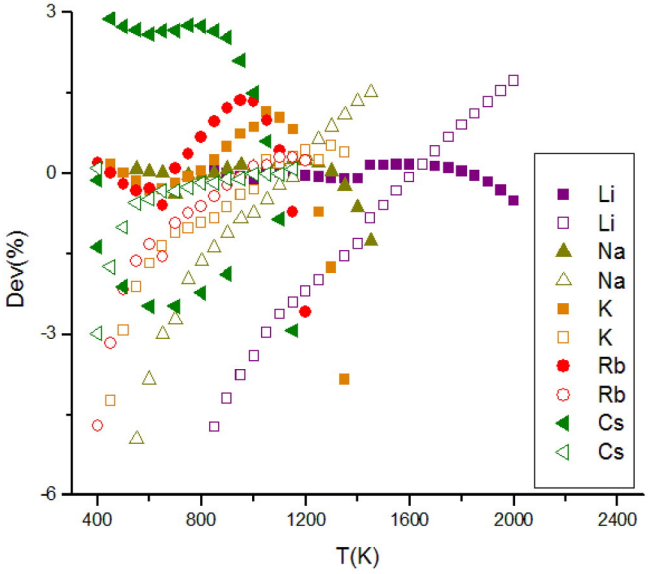

Fig. 1. Deviation plot from experimental data [18,24] for calculated liquid densities by this EOS as a function of temperature for alkali metals. The filled markers show the result of present EOS and the corresponding open ones from Mehdipour and Boushehri [25].