A perturbed hard-sphere equation of state for alkali metals

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Abstract

A perturbed hard-sphere equation of state, employing a basic frame proposed by Eslami [H. Eslami, J. Nucl. Mater. 336 (2005) 135–139] has been developed for alkali metals. Following the approach introduced by Ihm et al. [G. Ihm, Y. Song, E.A. Mason, J. Chem. Phys. 94 (1991) 3839–3848], the temperature dependence of the parameters a and b has been fitted to liquid density data for potassium. The scaling parameters that are used to reduce the temperature are the temperature and density at normal boiling point. The important improvement is to omit the adjustable parameters, the well depth and the location of the minimum of pair potential, which are required to apply the earlier equation of state of Eslami. The present EoS, which can be used without fitting parameters, reproduces the volumetric behavior of liquid alkali metals with a very good accuracy. Six hundred and ninety four data points at different pressures and temperatures are examined and the average absolute deviation of predicted liquid density data compared to experiment is 1.41%.
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1. Introduction

The knowledge of thermodynamic properties of liquid alkali metals is of considerable interest in industry. Liquid metals have a number of interesting characteristics, which make them applicable in high-temperature operations as heat transfer agents and reactor coolants. The most important characteristics of liquid alkali metals include high boiling points, extended liquid ranges, high thermal conductivities, low vapor pressures, and high enthalpies of vaporization. Accurate measurement of thermodynamic properties of metals is difficult due to high experimental temperatures and the reactivity of the melt with atmospheric components; in fact samples could be easily contaminated during measurements. In these circumstances the development of correlation procedures and equations of state to obtain thermodynamic properties is highly useful. Modern perturbation theories of liquids have been developed over the past four decades based on the recognition that the structure of dense fluids is determined primarily by the repulsive forces, so

that fluids of hard bodies (spherical or non-spherical) can serve as useful reference systems [1–5]. The influence of attractive forces can then be treated by statistical mechanical perturbation theory, as can the softness of the repulsions. Given the intermolecular forces it is now possible to predict thermodynamic properties of dense fluids from perturbation theories in their stable range of temperature and density [6]. An accurate equation of state for liquid metals, based on statistical mechanical perturbation theory, is recently proposed by Eslami et al. [7,8]. This equation includes two parts. A primary hard-sphere model and a perturbation part which introduces the van der Waals attractive term. Two temperature dependent parameters appear in this equation of state. $b(T)$ (the van der Waals co-volume) which is related to the volume of hard spheres and $a(T)$ which reflects the attraction between spheres. It has been shown that $a(T)$ and $b(T)$ are insensitive to the details of the potential energy function and when scaled in terms of proper characteristic parameters, are universal functions of the reduced temperature [9]. In his research, Eslami has applied two scaling factors, ε, the depth, and σ, the location of the minimum of the pair potential energy curve [7]. Because there is no reliable unique data for ε and σ of liquid alkali metals, these reducing factors should be considered as adjustable parameters.

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Table 1
Normal boiling point parameters for liquid alkali metals

Metal	T_{nb}^{12} (K)	ρ_{nb}^{12} (kg m^{-3})
Li	1616.2	402.8438
Na	1156.3	741.2224
K	1030.4	668.4011
Rb	960.4	1201.4209
Cs	942.3	1469.9476

Table 2
The calculation results for the saturated liquid alkali metals

Metal	ΔT (K)	NP[a]	AAD[b] (%)
Lithium	453.67–2800	24	2.21
Sodium	371.02–2400	23	1.22
Potassium	336.76–2200	18	0.76
Rubidium	312.46–1900	17	1.43
Cesium	301.63–1800	16	2.08

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

[b] $\text{AAD} = \frac{100}{\text{NP}} \sum\limits_{i=1}^{\text{NP}} \frac{|\rho_{i,\text{cal.}} - \rho_{i,\text{exp.}}|}{\rho_{i,\text{exp.}}}$.

Therefore they are determined by fitting to the experimental data.

In this work we show that it is possible to reduce a, b as functions of T with two easily available normal boiling point data (density, ρ_{nb} and temperature, T_{nb}). Hence, this equation of state can be used to predict the volumetric behavior of liquid alkali metals without further fitting of data.

2. Theory

The general frame for any perturbed equation of state is

$$Z = \frac{p}{\rho k T} = Z_{\text{ref.}} + Z_{\text{pert.}} \tag{1}$$

where the first term is given by a reference physical model such as hard-sphere or square well model and the second term is a perturbation term. In the PHS (perturbed hard-sphere) equation of state, which is proposed by Eslami et al. [7,8], the reference system used is a hard-sphere model and the attractive part of the van der Waals EoS is introduced for the perturbation term, i.e.:

$$Z_{\text{ref}} = Z_{\text{HS}} = 1 + b\rho g(d^+) \tag{2}$$

and

$$Z_{\text{pert.}} = -\frac{a\rho}{kT} \tag{3}$$

where d is the hard sphere diameter and $g(d^+)$ is the pair radial distribution function of hard spheres at contact, which is expressed by the Carnahan–Starling equation [10]:

$$g(d^+) = \frac{1 - \eta/2}{(1 - \eta)^3} \tag{4}$$

The packing fraction, η, is defined as

$$\eta = \frac{b\rho}{4} \tag{5}$$

Several procedures can be employed to determine the temperature dependent parameters $a(T)$ and $b(T)$. Generally, one may perform the integral equations derived by Song and Mason [11], which require the potential energy function, i.e.:

$$a(T) = 2\pi \int_0^\sigma (1 - e^{-\beta u_0}) r^2 \, dr \tag{6}$$

and

$$b(T) = 2\pi \int_0^\sigma [1 - (1 + \beta u_0) e^{-\beta u_0}] r^2 \, dr \tag{7}$$

where $\beta = 1/kT$, u_0 the repulsive part of the potential and r is the inter atomic distance.

This is the most accurate way, but unfortunately, there is no accurate intermolecular potential energy function available for liquid alkali metals.

Ihm et al. have found that $a(T)$ and $b(T)$ are insensitive to the details of potential energy curve [9]. Consequently, it is possible to use a general law of corresponding states which relates reduced forms of $a(T)$ and $b(T)$ to reduced temperature through universal functions [6,9]. Eslami has considered this law to predict the temperature dependent parameters of his EoS. $a(T)$ and $b(T)$ which have been reduced by $\varepsilon\sigma^3$ and σ^3, respectively are calculated as functions of the reduced temperature kT/ε. Since ε and σ, the characteristic parameters of the potential energy curve are not uniquely known for metals, Eslami has determined these factors by fitting the equation of state to experimental data. Therefore a very accurate semi-empirical EoS with just two empirically adjustable parameters has been developed. On the other hand, the overall P–ρ–T behavior of the liquid metal should be established to determine the scaling factors and utilize the equation of state. The purpose of this work is to omit the adjustable parameters and develop an equation of state with the least input information.

We require two parameters which scale for intermolecular energy and molecular sizes. It is known that the normal boiling point temperature is directly affected by molecular interactions. In other words, the normal boiling temperature is the temperature at which the fraction of molecules having sufficient kinetic energy to escape from intermolecular attractions make vapor pressure equal to 1 atm. Also the density of liquid at this point is obviously related to the molecular size. In fact, the molar volume at normal boiling temperature is just slightly larger than the volume of the molecules themselves. As another evidence Eslami et al. [8] have demonstrated that ε and σ^3 of many liquid metals correlate to T_{nb} (normal boiling point temperature) and ρ_{nb} (the density at normal boiling point), respectively. This also confirms our suggestion. Hence, we propose these two characteristic properties, T_{nb} and ρ_{nb}, as the first scaling candidates.

We define the following reduced parameters in which the parameter T is reduced by T_{nb} and ρ is reduced by ρ_{nb}, i.e.:

$$T_r = \frac{T}{T_{nb}} \tag{8}$$