An Analytical Equation of State for Alkaline Earth Metals

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In this work, an analytical equation of state based on statistical mechanical perturbation theory, which was initially developed for normal fluids and can be applied to predict the P–V–T data for saturated liquid alkaline earth metals, is presented. The equation of state is that of Ihm, Song, and Mason, and the temperature-dependent parameters of the equation of state are calculated from a corresponding-states correlation as functions of the reduced temperature. Two scaling constants are sufficient for this purpose, the surface tension and the liquid density at the melting point. The equation of state is used to predict the saturated liquid density of molten alkaline earth metals from the melting point up to 2000 K, for which experimental data exist, within an accuracy of 5%.

1. INTRODUCTION

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

In this work, an analytical equation of state based on statistical mechanical perturbation theory proposed by Song and Mason [1] is of

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special interest. Three temperature-dependent parameters arise in this equation of state: the second virial coefficient, B_2, an effective hard-sphere diameter, b, and a scaling factor for the pair distribution function, α. The first parameter is often available experimentally, and the other two parameters can be calculated by fitting the second virial coefficients to a simple potential energy function and using empirical formulas [2] or numerical tabulated results by Song and Mason [3]. This fact leads to a law of corresponding-states developed by Ihm et al. [3] that reduces the entire P–V–T surface of a normal fluid to a single curve of the effective pair distribution function at contact as a function of reduced density.

If the second virial coefficients are not known experimentally, there are several corresponding-states correlations by which the second virials can be calculated as a function of temperature with reasonable accuracy. Boushehri and Mason [4] developed a method for predicting the second virial coefficients, and hence the equation of state, from the heat of vaporization as the energy parameter for reducing temperature and the liquid density at the triple point as the size parameter for reducing second virial coefficients. In this method, the scaling parameters, the heat of vaporization and the liquid density at the triple point, are readily available at ordinary temperatures and pressures. Another correlation was proposed by Ghatee and Boushehri [5] to predict the equation of state for liquids from the surface tension and the liquid density at the freezing temperature. The accuracy of densities they predicted was about that of Tao and Mason [6], based on using the critical constants, but they removed the difficulty of rarely available critical constants.

In this paper, we adapt the correlation procedure by Ghatee and Boushehri [5] to calculate the temperature-dependent parameters of the equation of state for saturated liquid alkaline earth metals (Mg through Ba). It is shown that this procedure leads to an analytical equation of state which can predict the saturated liquid density of these metals from the melting point up to several hundred kelvins above the boiling point within $\pm 5\%$.

2. THEORY OF THE EQUATION OF STATE

Statistical mechanics provides us with the following equation, assuming a pair-wise additive central intermolecular potential [7],

$$\frac{P}{\rho kT} = 1 - (2\pi\rho/3kT) \int_0^\infty (\partial u/\partial r) g(r) r^3 \, \mathrm{d}r \tag{1}$$

where P is the pressure, ρ is the density, $g(r)$ is the pair distribution function, and $\partial u/\partial r$ is the derivative of the intermolecular potential, $u(r)$, with respect to distance, r. Applying the Weeks–Chandler–Andersen division for the potential energy function [8], Ihm et al. [3] derived the following equation,

$$\frac{P}{\rho kT} = 1 + B_2\rho + \alpha\rho[G(b\rho) - 1] \tag{2}$$

Here B_2 is the second virial coefficient, α is the repulsive contribution to the second virial coefficient, $G(b\rho)$ is the average pair distribution function at contact for equivalent hard spheres, and b is the analog of the van der Waals covolume and can be calculated from α by the following equation,

$$b = \alpha + T\frac{d\alpha}{dT} \tag{3}$$

All of the temperature-dependent parameters, B_2, α, and b, can be written in terms of the intermolecular pair potential as [1]

$$B_2 = 2\pi \int_0^\infty [1 - \exp(-u/kT)]r^2 \, dr, \tag{4}$$

$$\alpha = 2\pi \int_0^{r_m} [1 - \exp(-u_0/kT)]r^2 \, dr, \tag{5}$$

and

$$b = \frac{2}{3}\pi d^3 = 2\pi \int_0^{r_m} [1 - (1 + u_0/kT) \; exp(-u_0/kT)]r^2 \, dr \tag{6}$$

where d is the effective hard-sphere diameter and u_0 is the repulsive branch of u defined as [8]

$$u_0(r) = \begin{cases} u(r) + \varepsilon, & r \leqslant r_m, \\ 0, & r > r_m, \end{cases} \tag{7}$$

Here, ε is the potential well-depth and r_m is the position of the minimum in u.

Ihm et al. [3] used the Carnahan–Starling equation for $G(b\rho)$ [9] and performed a correction in Eq. (2) for the attractive forces to obtain

$$\frac{P}{\rho kT} = 1 - \frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{8}$$

where λ is an adjustable parameter. From Eqs. (2) and (8), $G(b\rho)$ can be written as

$$G(b\rho)^{-1} = (1 - \lambda b\rho) = \alpha\rho \left[\frac{P}{\rho kT} - 1 + \frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} \right] \qquad (9)$$

which immediately implies a principle of corresponding states, since plots of G^{-1} vs. $b\rho$ yield very nearly straight lines with various slopes, $-\lambda$, for different fluids [3].

As mentioned earlier, knowledge of accurate potential energy functions or the experimental second virial coefficients are necessary for the calculation of B_2, α, and b in Eq. (8). But, for the second group elements, neither an accurate potential function nor experimental values of $B_2(T)$ are known. To calculate the second virial coefficient, we utilized a corresponding-states correlation proposed by Ghatee and Boushehri [5], based on the surface tension and the liquid density at the melting point for normal fluids. The correlation reads as

$$B_2^*(T) = 0.0804 - 2.1288 T^{*-1} - 8.5597 T^{*-2}$$
$$+ 7.4294 T^{*-3} - 3.3494 T^{*-4} \qquad (10)$$

with

$$T^* = \left[T^{3/2} / (T_{\text{ref}} T_{\text{m}}^{1/2}) \right]^{3/4}, \qquad (11)$$

$$T_{\text{ref}} = \frac{\sigma_{\text{m}} \rho_{\text{m}}^{-2/3} N^{1/3}}{R}, \qquad (12)$$

and

$$B_2^* = B_2(T) \rho_{\text{m}} \qquad (13)$$

where σ is the surface tension, N is Avogadro's number, R is the universal gas constant, and the subscript m refers to the melting point. Ghatee and Boushehri [5] rescaled the empirical formulas by Song and Mason [2] for α and b to obtain the following equations:

$$\alpha\rho_{\text{m}} = a_1 \left[\exp\left(-c_1 T^*\right) \right] + a_2 \left[1 - \exp\left(-c_2(T^*)^{-1/4}\right) \right] \qquad (14)$$

and

$$b\rho_{\text{m}} = a_1 \left[1 - c_1 T^* \right] \exp\left(-c_1 T^*\right)$$
$$+ a_2 \left[1 - \left(1 + 0.25 c_2(T^*)^{-1/4}\right) \exp\left(-c_2(T^*)^{-1/4}\right) \right] \qquad (15)$$

where
$$a_1 = -0.01054 \quad c_1 = 0.7613$$
$$a_2 = 2.9387 \quad c_2 = 1.3227$$
In this work, we will use the correlations of Eqs. (10) – (15) to calculate the temperature-dependent parameters of the equation of state.

3. RESULTS AND DISCUSSION

We have used Eq. (8) for the calculation of the liquid density of alkaline earth metals. The temperature-dependent parameters, B_2, α, and b, are calculated using Eqs. (10)–(15). Knowing the temperature-dependent parameters of the equation of state, one parameter remains, λ, which can be calculated by knowing experimental P–V–T data. Once the value of the constant λ is determined, the entire volumetric behavior of the fluid is established. Values of λ, obtained from regression of experimental data, as well as the surface tension and liquid densities at the normal melting point for alkaline earth metals, are given in Table I.

We have calculated the saturated liquid densities of Mg, Ca, Sr, and Ba from the melting point up to 2000 K, for which experimental data are reported by Bystrov et al. [10] as correlating equations. The results are listed in Table II and are compared with experiment [10]. Although the results listed in Table I show the degree of consistency between our model and experimental data, the results for magnesium as a typical example are also shown in Fig. 1, on which any deviation pattern is more obvious. Since the present equation of state is based on a mean-field approximation, it does not work accurately in the two-phase and nonanalytical critical region. Therefore, we can not accurately calculate the vapor-pressure curve via the present equation of state.

In summary, an equation of state for alkaline earth metals was developed based on statistical mechanical theory. The temperature-dependent parameters were calculated from the extrapolation of normal fluids' corresponding-states correlations to the metallic region. The fact that the

Table I.   Parameters used for Alkaline Earth Metals [10]

Metal	T_m (K)	ρ_m (mol·L^{-1})	σ_m (N·m^{-1})	λ
Mg	923	65.4186	0.5770	0.456
Ca	1114	34.3782	0.3248	0.438
Sr	1041	26.8105	0.2896	0.434
Ba	1000	24.3010	0.2665	0.428

Table II. Comparison of Calculated and Experimental [10] Values
of Liquid Densities

| | | Density (mol·L^{-1}) | | |
| | | Calc. | Expt. | |
T (K)	P (bar)	Calc.	Expt.	Dev (%)
Magnesium				
923	3.586×10^{-3}	64.37	65.42	−1.60
1000	1.483×10^{-2}	64.37	64.60	−0.36
1100	6.288×10^{-2}	64.06	63.36	1.10
1200	0.207	63.43	62.54	1.42
1300	0.5616	62.54	61.30	2.02
1400	1.309	61.45	60.07	2.29
1500	2.705	60.23	59.25	1.65
1600	5.070	58.95	58.01	1.62
1700	8.774	57.63	56.78	1.50
1800	14.21	56.31	55.96	0.62
1900	21.77	54.98	54.72	0.47
2000	31.82	53.66	53.90	-0.44
Calcium				
1114	2.056×10^{-3}	34.94	34.45	1.42
1200	6.876×10^{-3}	34.57	33.95	1.83
1300	2.307×10^{-2}	34.01	33.38	1.88
1400	6.470×10^{-2}	33.36	32.80	1.71
1500	0.1572	32.66	32.23	1.33
1600	0.3401	31.93	31.65	0.88
1700	0.6688	31.18	31.08	0.32
1800	1.215	30.44	30.50	−0.19
1900	2.066	29.70	29.93	−0.76
2000	3.321	28.96	29.35	−1.33
Strontium				
1041	2.504×10^{-2}	27.68	26.81	3.24
1100	6.069×10^{-2}	27.56	26.79	2.87
1200	2.204×10^{-2}	27.25	26.67	2.17
1300	6.491×10^{-2}	26.83	26.46	1.40
1400	0.1621	26.33	26.19	0.53
1500	0.3554	25.79	25.88	−0.35
1600	0.701	25.23	25.55	−1.25
1700	1.267	24.65	25.21	−2.22
1800	2.133	24.08	24.86	−3.13
1900	2.381	23.50	24.51	−4.10
2000	5.093	22.99	24.16	−4.84
Barium				
1000	7.055×10^{-5}	25.48	24.30	4.86
1100	3.931×10^{-4}	25.28	24.08	4.98
1200	1.615×10^{-3}	24.96	23.87	4.57

Table II.   (*Continued*)

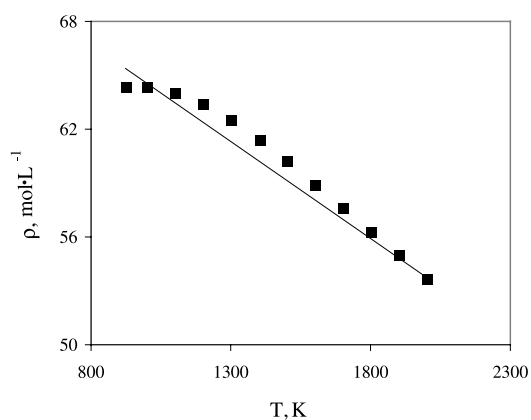| T (K)	P (bar)	Density (mol·L^{-1})		Dev (%)
		Calc.	Expt.	
1300	5.264×10^{-3}	24.54	23.65	3.76
1400	1.432×10^{-2}	24.05	23.43	2.65
1500	3.373×10^{-2}	23.53	23.21	1.38
1600	7.081×10^{-2}	22.99	22.99	0.00
1700	0.1353	22.45	22.78	−1.45
1800	0.2393	21.91	22.56	−2.88
1900	0.3970	21.38	22.34	−4.29
2000	0.6239	20.84	22.12	−5.78

Fig. 1. Comparison of calculated (■) and experimental (——) saturated liquid density of magnesium vs. temperature.

second virial coefficients of metals obey the law of corresponding states may be unexpected. However, Eqs. (10)–(15) for B_2, α, and b based on a corresponding-states correlation with the surface tension and the liquid density at the 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 experimental $P–V–T$ data. This work indicates that only two characteristic constants, the liquid density and the surface tension at the melting point, are sufficient to predict the liquid density of alkaline earth metals, without knowing the

whole potential energy curve or the experimental second virial coefficients of these metals.

REFERENCES

1. Y. Song and E. A. Mason, *J. Chem. Phys.* **91**:7840 (1989).
2. Y. Song and E. A. Mason, *Fluid Phase Equilib.* **75**:105 (1992).
3. G. Ihm, Y. Song, and E. A. Mason, *J. Chem. Phys.* **94**:3839 (1991).
4. A. Boushehri and E. A. Mason, *Int. J. Thermophys.* **14**:685 (1993).
5. M. H. Ghatee and A. Boushehri, *Int. J. Thermophys.* **17**:945 (1996).
6. F. M. Tao and E. A. Mason, *Int. J. Thermophys.* **13**:1053 (1992).
7. D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).
8. J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**:5237 (1971).
9. N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**:635 (1969).
10. P. I. Bystrov, D. N. Kagan, G. A. Krechetova, and E. E. Shpilrain, *Zhidrometallicheskie Teplonositeli Dlya Teplovgh Trubi Energeticheskih (Liquid Metal Heat-Carriers for Heat Pipe Facilities)* (Nauka Press, Moscow, 1988).