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Abstract
The perturbed Lennard-Jones chain (PLJC) equation of state is formulated based
on first-order variational perturbation theory. The model uses two parameters
for a monatomic system, segment size, σ, and segment energy, ε/k. In this
work, we employed the PLJC equation to calculate the liquid density of 26
metals, including alkali and alkali earth metals, iron, cobalt, nickel, copper,
silver, gold, zinc, cadmium, mercury, aluminium, gallium, indium, thallium,
tin, lead, antimony, and bismuth, for which accurate experimental data exist in
the literature. The calculations cover a broad range of temperatures ranging
from the melting point to close to the critical point and pressures ranging from
the vapour-pressure curve up to pressures as high as 2000 bar. The average
absolute deviation in the liquid density predicted by the PLJC equation of state
in the saturation line compared with experimental data is 1.26%. Also, using
the normal melting temperature and liquid density at melting point (T_m, ρ_m) as
input data for the estimation of the equation of state parameters provides a good
correlation of liquid density at saturated and compressed pressures.

1. Introduction

Metals, both in liquid and in vapour states, are complicated in structure. Information
on physical and thermodynamic properties of these groups of elements is important in
technological application. Alkali metals, because of their good heat transfer and nuclear
properties, are used as coolants in fast reactors. They are also used commonly as reducing
agents in the pharmaceutical, perfumery and general chemical industries. Their ability to react
with air and water is a strong disadvantage [1]. The high critical temperature and high toxicity
make liquid metals challenging systems to investigate experimentally [2]. These considerations
also make the metals suitable candidates for theoretical investigation.

The description of properties of fluids using accurate equations of state is considered an
efficient tool for the calculation of thermodynamic properties. The hard-sphere fluid is taken

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Table 1. PLJC characteristic parameters of metals.

Metal	ΔT (K)	σ (nm)	ε/k (K)	NP[a]	% AAD[b] from $(\varepsilon/k, \sigma)$[c]	% AAD from correlation[d]	References
Lithium	454–2500	3.05	2996	32	0.64	3.06	[16]
Sodium	371–2400	3.69	2006	22	2.07	3.83	[16, 17]
Potassium	371–2000	4.53	1714	28	1.77	2.53	[16]
Rubidium	313–2000	4.86	1618	27	2.67	2.39	[16]
Caesium	302–1900	5.21	1531	26	2.12	5.95	[16]
Magnesium	923–2000	3.15	4072	12	0.27	5.76	[15]
Calcium	1114–2000	3.90	4850	10	0.96	5.19	[15]
Strontium	1041–2000	4.31	6819	11	0.57	3.45	[15]
Barium	1000–2000	4.50	7950	11	0.90	6.48	[15]
Iron	1808–3003	2.58	9122	14	1.73	7.32	[19]
Cobalt	1765–3000	2.55	9000	14	2.30	8.14	[19]
Nickel	1728–3000	2.54	9200	14	2.82	9.21	[19]
Copper	1356–2903	2.44	6780	18	0.25	7.87	[19]
Silver	1234–2253	2.89	6500	12	0.51	3.56	[19]
Gold	1336–2983	2.90	9128	18	0.72	1.72	[19]
Zinc	693–1000	2.82	5880	5	0.32	3.23	[15]
Cadmium	594–1000	3.15	4669	6	0.60	3.30	[15]
Mercury	273–1073	3.30	5389	25	0.68	9.64	[15, 16]
Aluminium	934–2335	2.85	4287	16	0.36	5.31	[19]
Gallium	303–1000	2.96	3970	8	2.76	7.80	[15]
Indium	430–1100	3.27	3500	8	2.85	4.58	[15]
Thallium	577–1000	3.34	3200	6	1.80	1.86	[15]
Tin	623–873	3.42	5960	6	0.64	3.07	[18]
Lead	670–970	3.47	3440	7	1.05	4.99	[18]
Antimony	904–1093	3.31	3090	7	0.72	4.62	[19]
Bismuth	642–872	3.60	3900	6	0.75	4.23	[18]
Average					1.26	4.97	

[a] NP is the number of data points.
[b] $\%\text{AAD} = \frac{100}{\text{NP}} \sum_{i=1}^{\text{NP}} |\rho_{i,\text{Calc.}} - \rho_{i,\text{Expt.}}|/\rho_{i,\text{Expt.}}$
[c] %AAD, when using the fitted $(\varepsilon/k, \sigma)$.
[d] %AAD, when using the predicted $(\varepsilon/k, \sigma)$ from equations (7) and (8).

into account as a reference system and the influence of the attractions and the softness of repulsions are considered as perturbations in statistical–mechanical perturbation theories [3, 4] of fluids. Additionally, attempts have been made to develop new integral equations [5].

In this work, we present the perturbed Lennard-Jones chain (PLJC) equation of state [6] for liquid metals. This equation belongs to a class of theoretically based equations of state that are formulated based on continuum space (as opposed to lattice space) liquid state perturbation theories. The theoretical foundation of the PLJC equation is a first-order variational theory for Lennard-Jones molecules [7, 8]. Like other perturbation-theory-based models, for a monatomic system it consists of two temperature-independent parameters: segment size σ, and non-bonded segment energy ε/k, where k represents the Boltzmann constant. The PLJC equation relates the pressure, temperature and density. We used the PLJC equation to quantify the volumetric properties of metals, and obtained best-fit values of model parameters. An comparison with other equations of state [9, 10] the PLJC equation predicted not only the saturated liquid density but also curves for compressed density.

Table 2. The calculation results for the compressed liquid density of metals.

Metal	ΔT (K)	Δp (bar)	NP	%AAD from $(\varepsilon/k, \sigma)$[a]	%AAD from correlation[b]	References
Lithium	600–1600	100–1000	18	1.62	2.90	[21–24]
Sodium	400–1600	100–1000	43	2.00	1.69	[21–24]
Potassium	600–1000	100–1000	12	2.37	2.35	[21–24]
Rubidium	600–1000	100–1000	12	3.83	4.50	[21–24]
Caesium	600–1000	100–1000	12	3.46	4.53	[21–24]
Tin	722–931	1000–2000	9	2.06	1.75	[18]
Lead	669–921	1000–2000	11	3.27	1.50	[18]
Bismuth	667–869	1000–2000	7	4.84	0.88	[18]
Mercury	290–427	1000–2000	16	0.51	1.50	[15, 16]
Average				2.66	2.40	

[a] %AAD, when using the fitted $(\varepsilon/k, \sigma)$.
[b] %AAD, when using the predicted $(\varepsilon/k, \sigma)$ from equations (7) and (8).

Table 3. The calculation results for the saturated liquid density of metals.

Metal	ΔT (K)	NP	%AAD This work	%AAD Previous works [9, 10]
Lithium	454–2500	32	0.64	0.88
Sodium	371–2400	22	2.07	2.79
Potassium	371–2000	28	1.77	2.27
Rubidium	313–2000	27	2.67	3.56
Caesium	302–1900	26	2.12	3.60
Magnesium	923–2000	12	0.27	1.26
Calcium	1114–2000	10	0.96	1.17
Strontium	1041–2000	11	0.57	2.37
Barium	1000–2000	11	0.90	3.33
Mercury	273–1073	25	0.68	1.07
Tin	623–873	6	0.64	2.20
Lead	670–970	7	1.05	3.27
Bismuth	642–872	6	0.75	1.85
Average			1.16	2.28

2. Analytical perturbed Lennard-Jones chain (PLJC) equation of state

The PLJC equation of state model presented here is based on the first-order variational perturbation theory for Lennard-Jones chains (LJCs), and was developed by O'Lenick and Chiew [7] and von Solms *et al* [8, 11–14]. In this theoretical treatment, the potential is separated into reference hard-sphere and attractive perturbation parts. Recently, this equation of state has been successfully applied to modelling simple and chain-like molecular fluids such as alkenes, aromatics and other hydrocarbons [6].

The PLJC equation of state is obtained from the Helmholtz energy via the standard thermodynamic relation [7, 8]:

$$\frac{p}{\rho kT} = \left(\frac{p}{\rho kT}\right)^{\text{REF}} + \left(\frac{p}{\rho kT}\right)^{\text{PERT}} \tag{1}$$
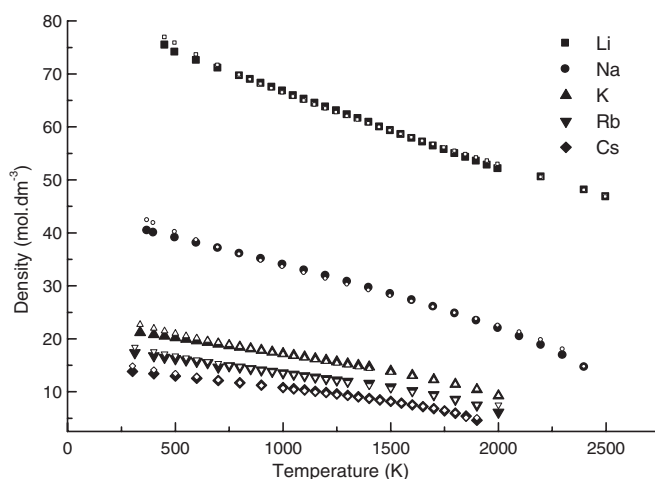
Figure 1. Comparison between calculated and experimental results for saturated liquid density of alkali metals. The open markers show the results of the present equation of state and the corresponding filled ones are experimental data [15–17].
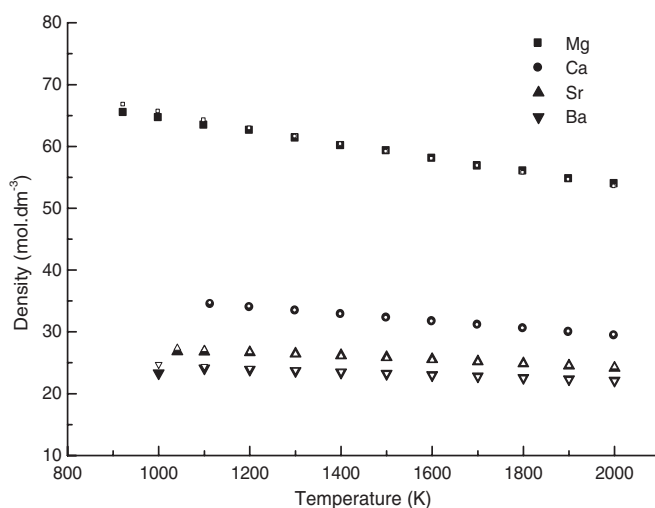

Figure 2. The same as figure 1 for alkali earth metals.

$$\left(\frac{p}{\rho kT}\right)^{\text{REF}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \tag{2}$$

$$\left(\frac{p}{\rho kT}\right)^{\text{PERT}} = \frac{12\eta}{(\varepsilon/kT)a^6} J_A(\eta) + \frac{12\eta}{(\varepsilon/kT)a^6}\left(\frac{1}{a^6} - 1\right) J_B(\eta) \tag{3}$$

$$J_A(\eta) = -1.8857\eta^2 - 1.6791\eta - 0.8903 \tag{4}$$

$$J_B(\eta) = 5.3559\eta^2 + 1.5227\eta + 0.4530. \tag{5}$$

Here, ε and σ represent the characteristic energy and size of segments; ρ is density; and the dimensionless parameter $a = d/\sigma$, where d is the diameter of the reference hard-sphere segment. The diameter d is state dependent and can be expressed as a function of absolute
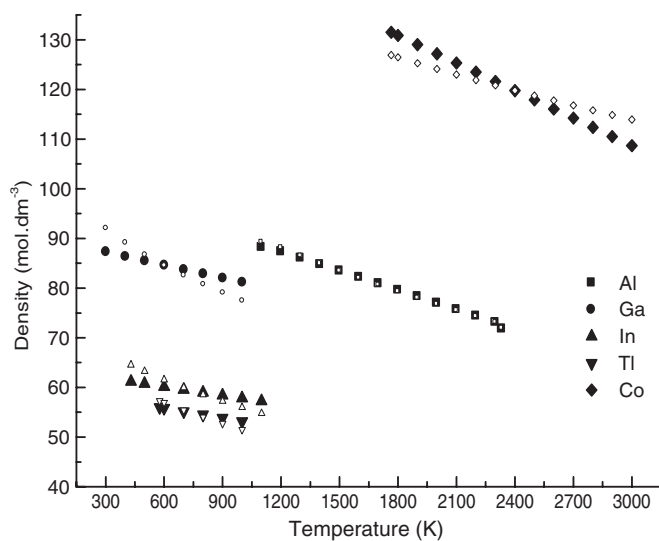
Figure 3. The same as figure 1 for Al, Ga, In, Tl, and Co.

temperature T:

$$\left(\frac{2^{1/6}}{a} - 1\right)^3 = 0.001\,126\frac{kT}{\varepsilon} + 0.001\,582. \tag{6}$$

In the above equations, the quantity $\eta = \pi\rho d^3/6$. The PLJC equation of state [6] is given by equations (1)–(6).

3. Results and discussion

The PLJC equation of state is applied to metals in a wide range of pressure. All metallic systems are considered as monatomic systems. Therefore, knowing two adjustable parameters σ and ε/k is sufficient to predict the equation of state for liquid metals. The PLJC equation of state is used to model the saturation line of metal systems. Experimental data are taken from [15–24]. The PLJC equation is found to fit the saturated liquid density very well over wide ranges of temperature and pressure. Table 1 shows regressed values (ε/k, σ) of PLJC parameters. Knowing the values of ε/k and σ, equation (1) can predict the PVT properties of liquid metals. We have calculated the liquid density in a wide range of temperatures and pressures, for which the experimental data are available in the literature. The results are tabulated in tables 1 and 2. As shown in tables 1 and 2, the agreement of our calculations with experiment is remarkable. The overall average deviation for the 26 metals studied here is only 1.26% when using the fitted (ε/k, σ).

We compared the PLJC equation with previous works [9, 10]. We will not reproduce these equation here, since they can be found in the reference cited [9, 10]. The deviations are displayed in table 3. On average, the PLJC equation yields the smaller percentage. In figures 1–5 correlations for the metals are shown in the temperature–density diagram. The results show that the model is able to describe the saturated liquid density data for metals. The equation of state is also employed to calculate the compressed liquid density of metals over a wide pressure range. The results are reported in table 2. The calculations cover a broad range of temperatures
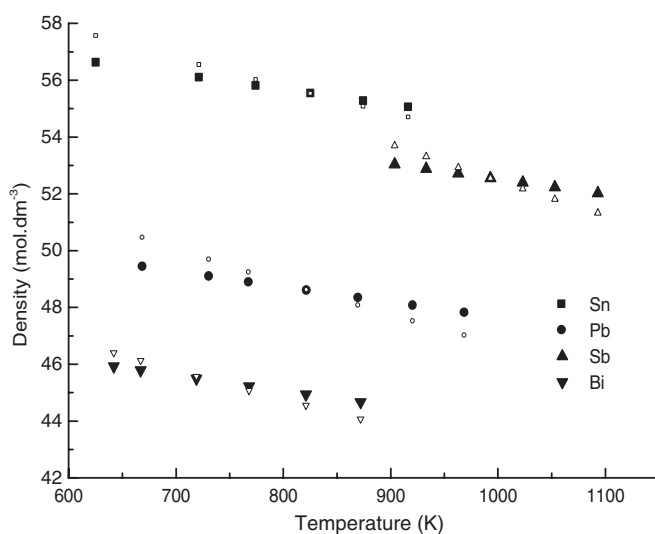
Figure 4. The same as figure 1 for Sn, Pb, Sb, and Bi.
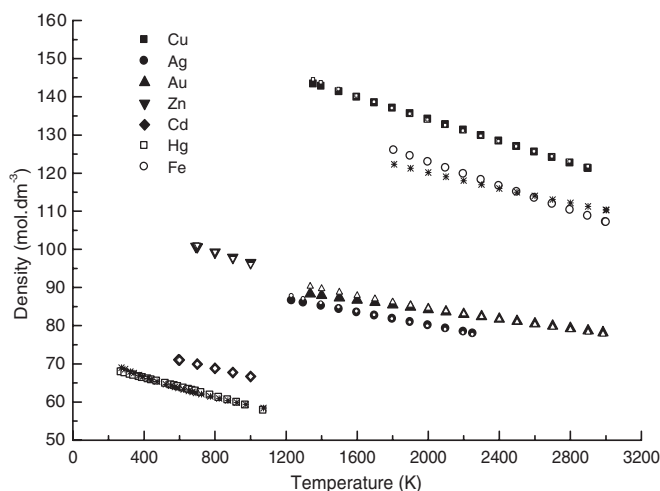

Figure 5. The same as figure 1 for Cu, Ag, Au, Zn, Cd, Hg, and Fe.

and pressures ranging from 100 up to 2000 bar. The average absolute deviation in the liquid density predicted by the PLJC equation of state compared with experimental data is 2.66%.

Figures 6 and 7 show for the equation of state parameters (ε, σ) that there is a systematic dependence of the parameters on the physical properties. In figure 6 the values of ε/k determined here are plotted versus the melting temperatures. Normally one finds that ε/k for a class of substances correlates with the critical temperatures, but unfortunately these are not known for most of the metals [25]. However, various theories of melting [26] indicate that the melting point should be proportional to ε. In figure 7 the values of σ determined here are plotted versus r and can be calculated from the liquid density at the melting point. In figure 7 it is seen that a very satisfactory correlation exists. Therefore, according to the law of corresponding states the values of ε, for different metals correlate with the melting temperatures (T_m) and the σ values correlate with the melting densities (ρ_m). To check the degree of accuracy of
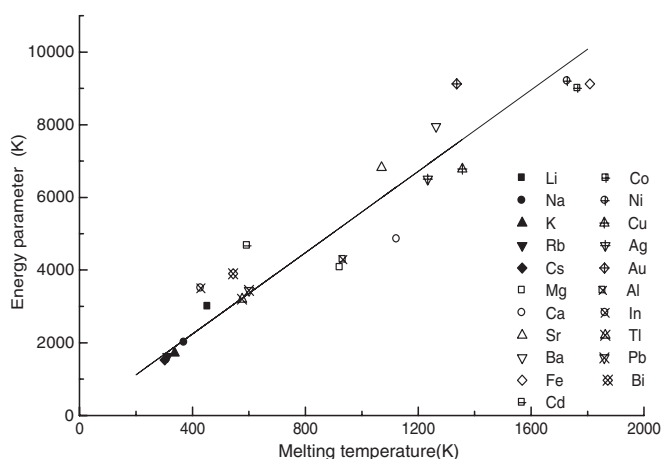
Figure 6. The correlation of the energy parameter ε/k with the melting temperature. The line represents the relationship $\varepsilon/k = 5.60T_{\mathrm{m}}$.
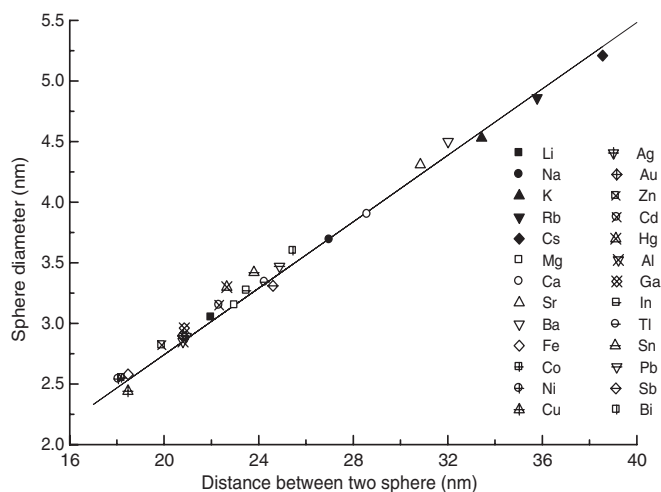

Figure 7. The correlation of the sphere diameter, σ, with the separation distance between two sphere centres, r. r is defined as $r = (\frac{3}{2\pi N_{\mathrm{Av}}\rho_{\mathrm{m}}})^{1/3}$ (ρ_{m} is the liquid density at the melting point, and N_{Av} is the Avogadro constant). The line represents the relationship $\sigma = 0.1371r$.

the correlations based on the normal melting point data of metals (figures 6 and 7), we have used the normal melting point data to predict their liquid densities at saturation and compressed pressures. These calculations show that the equation of state for liquid metals would also be predictable with accuracy using normal melting point data and liquid density at the melting point $(T_{\mathrm{m}}, \rho_{\mathrm{m}})$ as input data. The relationships between the parameters ε and σ, with the temperature and liquid density at the melting point represented by the line in figures 6 and 7, can be expressed as

$$\frac{\varepsilon}{k} = 5.60T_{\mathrm{m}} \tag{7}$$

$$\sigma = 0.1371r \tag{8}$$

where $r = (\frac{3}{2\pi N_{\mathrm{Av}}\rho_{\mathrm{m}}})^{1/3}$.

In tables 1 and 2, the average absolute deviation, when using the predicted $(\varepsilon/k, \sigma)$ from equations (7), and (8), for liquid density at saturation and at compressed pressures for 26 metals are 4.95% and 2.40%, respectively.

There exist some similarities between fluid metals and ordinary fluids that lead us to check the present equation of state for them. For example, liquid metals can be treated as simple monatomic systems and like normal fluids. The perturbed Lennard-Jones chain (PLJC) equation of state was proposed and applied to estimate the liquid density of metals up to the critical point for alkali metals and boiling temperature for other cases. Model parameters σ and (ε/k) were obtained by regressing saturated liquid density data. The PLJC equation was found to estimate saturated liquid density and compressed liquid density for metals accurately over wide ranges of pressure and temperature. Using a different approach for the estimation of the equation of state parameters provides a good correlation of liquid density at saturated and compressed pressures.

Acknowledgment

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