RESEARCH ARTICLE

Ability of the generalized van der Waals and Berthelot equations of state to determine the thermodynamic stability of liquid lead

Ramesh Arumugam, Balasubramanian Ramasamy*

Department of Physics, Arignar Anna Government Arts College, Namakkal 637 002, Tamilnadu, India

The known van der Waals and Berthelot equations of state do-not precisely describe the thermodynamic properties of fluids. To improve its accuracy, the attractive term of the van der Waals equation of state has been modified in six different ways. These generalized equations of state have been employed to determine the spinodal (thermodynamic stability boundary) and the thermodynamic limit of superheat of liquid lead. The equations of state are rewritten in reduced form, from which follows the law of corresponding states. The appropriate modification of the attractive term of the equation of state yielding the value of thermodynamic limit of superheat agreeing with the experimental value for lead has been established. It has been established that liquid lead can be superheated, under rapid heating, up to a temperature 4565 K. That is, liquid lead can be superheated to 2544 K above the normal boiling temperature. At the thermodynamic limit of superheat, the volume of the liquid lead is 4.0095×10^{-5} $m^3 mol^{-1}$. This fact is to be taken into account when liquid lead is subjected to rapid heating.

Keywords: Corresponding states, critical point, equation of state, lead, spinodal, thermodynamic limit of superheating.

Introduction

The study of the thermodynamic properties of lead is of scientific and technological significance. The experimental studies on the thermodynamic properties of the lead in the metastable region, encounter severe difficulties. Thus, arises a need for theoretical studies on the thermodynamic properties of lead in the metastable region. In recent years, several studies have been made on the thermodynamic properties of lead.[1-9] This fact manifested the relevance of the study of the thermodynamic properties of lead. One of the statistical-mechanical and thermodynamical approaches to study the thermodynamic properties of substance is the development of equation of state for substances. To improve the accuracy, the known equations of state are generalized by modifying the attractive terms.[10-19]

The physical properties of lead are melting temperature $T_m = 600.6$ K, boiling temperature $T_b = 2021$ K, critical temperature $T_c = 5000$ K, critical pressure $P_c = 180$ MPa, critical density $D_c = 3250$ Kgm^{-3}, critical volume $V_c = 6.3754 \times 10^{-5} m^3 mol^{-1}$,

critical compressibility Z_c = 0.2761 and thermal conductivity σ_T = 47.7 Wm^{-1}K^{-1}. This work is aimed at developing a new equation of state for lead in the metastable state. In the technological processes such as laser ablation, wire explosion and cooling the fast-neutron nuclear reactors, lead undergoes rapid heating. This results in the superheating of liquid lead to temperatures above its equilibrium boiling temperature. However, there is a limit in temperature up to which the liquid lead can be superheated at a given pressure. The temperature of superheat, under zero pressure, is the thermodynamic limit of superheat. The superheated lead is in a metastable state which on the phase diagram lies between the binodal and the spinodal. The performance characteristics of the modified equations of state in describing the properties of lead in the metastable state are investigated. In this respect, the known van der Waals and Berthelot equations of state are modified by incorporating new parameters in their attractive terms.

Generalized Equations of State

The known van der Waals and Berthelot equation of state do not precisely describe the thermodynamic properties of fluids.[20,21] This may be attributed to the inaccurate attractive terms in these equations of state. Hence, new equation of state is proposed by introducing new parameters in the attractive term. Such modified equations of state for one mole of substance have the form:

$$P = \frac{RT}{V-b} - \frac{a}{T^m(V+c)^n} \tag{1}$$

Where P = Pressure; V = Molar volume; T = Temperature; R = Universal gas constant; a, b, c, m and n are substance-specific parameters. Four special cases of Eq. (1) with $m = 0$, $m = 1$, $m = \frac{1}{2}$ and $c=b$ are also considered. The parameters a, b, c, m and n of the modified Berthelot equation of state are determined through the critical-point parameters.

The vapor-liquid critical point conditions are

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{2}$$

Application of the critical-point conditions to the equation of state given by Eq. (1) gives the critical volume, critical temperature and critical pressure as

$$V_c = \frac{[(n+1)b+2c]}{(n-1)} \tag{3}$$

$$T_c = \left[\frac{4na(n-1)^{n-1}}{R(n+1)^{n+1}(b+c)^{n-1}}\right]^{\frac{1}{m+1}} \tag{4}$$

$$P_c = \left[\frac{aR^m(n-1)^{m+n}(n-1)^{m+1}}{2^{2m}n^m(n+1)^{n+1}(b+c)^{m+n}}\right]^{\frac{1}{m+1}} \tag{5}$$

When Eqs. (3)-(5) are taken into account, we get the critical compressibility factor as

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{(n-1)[(n+1)b+2c]}{4n(b+c)} \tag{6}$$

Equations-of–state Parameters

Eq. (6) may be rearranged as

$$n^2 b - [4(b+c)Z_c - 2c]n - (b+2c) = 0 \tag{7}$$

The parameters a, b, c and n of the modified Berthelot equation of state are determined through the critical–point parameters. Eq. (7) is a quadratic equation with respect to the parameter n. The physically meaningful solution (i.e. $n>0$) of Eq. (7) is

$$n = \left(2Z_c + \frac{2cZ_c}{b} - \frac{c}{b}\right) + \sqrt{\left(2Z_c + \frac{2cZ_c}{b} - \frac{c}{b}\right)^2 + \left(\frac{2c}{b}+1\right)} \tag{8}$$

Eq. (3) may be rearranged as

$$(n-1)V_c = [(n+1)b+2c] \tag{9}$$

From Eqs. (3)-(6), we get the expressions for the equation-of-state parameters as

$$a = \frac{RT_c^{\frac{1}{m+1}}(n+1)^{n+1}(b+c)^{n-1}}{4n(n-1)^{n-1}} \tag{10}$$

$$b = \left[1 - \frac{(n-1)}{2nZ_c}\right]V_c \tag{11}$$

$$c = \left[\frac{(n^2-1)}{4nZ_c} - 1\right]V_c \tag{12}$$

Using Eqs. (8), (10), (11) and (12) the parameters a, b, c and n of the modified Berthelot equation of state can be determined. Moreover, using the Riedel's parameter, the value of the parameter m can be determined.

The modified equation of state may be rewritten in terms of the reduced variables as

$$P^* = \frac{1}{(n-1)}\left[\frac{4n(b+c)T^*}{[(n+1)b+2c]V^* - b(n-1)}\right.$$

$$\left. - \frac{(b+c)^n(n+1)^{n+1}}{T^{*m}[(n+1)b+2c]V^* + c(n-1)]^n}\right] \tag{13}$$

Where $P^* = P/P_c$; $V^* = V/V_c$; $T^* = T/T_c$

Riedel's parameter is defined as

$$\alpha_R = \left(\frac{\partial P^*}{\partial T^*} \right)_{V^*}, \text{ at critical point} \tag{14}$$

From Eqs. (13) and (14), we get

$$\alpha_R = \frac{(m+2)n + m}{n-1} \tag{15}$$

Eq. (15) may be rearranged to get the expression for m as

$$m = \frac{(n-1)\alpha_R - 2n}{n+1} \tag{16}$$

The reduced equation of state given by Eq. (13) represents the four-parameter law of corresponding states with the thermodynamic similarity parameters b, c, m and n. That is, substances obeying the modified Berthelot equation of state, with the same values of the parameters b, c, m and n are thermodynamically similar. That is, such substances have similar intermolecular force characteristics.

Spinodal

The knowledge of the spinodal, a characteristic curve on the phase diagram, is essential in describing the properties of a substance in the critical and in the metastable states. Fig 1 schematically depicts[22] the vapor-liquid equilibrium curve (binodal) and the stability boundary curve (spinodal) of substances.
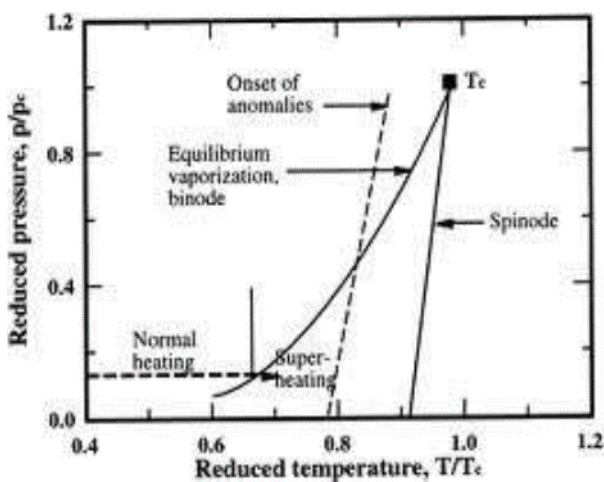

Figure 1 | Schematic phase diagram of substances.[23]

The spinodal defines the thermodynamic stability boundary of the phase envelope. The spinodal encloses the region of unstable states for which the isothermal elasticity is negative. For stable states, the isothermal elasticity is positive. In the region between the binodal and the spinodal on the phase diagram, the liquid is in the metastable state. Considering the scientific and technological significance, in recent years, several studies have been made on the behavior of the superheated metastable fluids.[23-32]

The spinodal is defined by the condition:

$$-\left(\frac{\partial P^*}{\partial V^*} \right)_{T^*} = 0 \tag{17}$$

Applying the condition given by Eq. (17) to Eq. (13), we get the equation of spinodal in T^*, V^* coordinates as

$$T_s^* = \left[\frac{(n+1)^{n+1}(b+c)^{n-1}\left[[(n+1)b + 2c]V_s^* - b(n-1) \right]^2}{4\left[[(n+1)b + 2c]V_s^* + c(n-1) \right]^{n+1}} \right]^{\frac{1}{m+1}} \tag{18}$$

Substituting Eq. (18) into Eq. (13), we get the equations of spinodal in P^*, V^* coordinates as

$$P_s^* =$$

$$\left[\frac{4^m(b+c)^{m+n}(n+1)^{n+1}\left[[(n+1)b + 2c]V_s^* - (nb+c) \right]^{m+1}}{\left[[(n+1)b + 2c]V_s^* + c(n-1) \right]^{2m}\left[[(n+1)b + 2c]V_s^* + c(n-1) \right]^{n+1}} \right]^{\frac{1}{m+1}} \tag{19}$$

With a decrease in pressure, the superheat of substances increases. Under zero pressure, the substance may be superheated to a maximum temperature above its normal boiling temperature. This is known as the thermodynamic limit of superheating.

Applying the condition $P = 0$ to Eq. (19), we get the expression for the reduced volume $V_{s,0}^*$ of the liquid at thermodynamic limit of superheat as

$$V_{s,0}^* = \frac{nb+c}{[(n+1)b + 2c]} \tag{20}$$

Substituting Eq. (20) into Eq. (18), we get

$$T_{s,0}^* = \left[\frac{(n+1)^{n+1}}{4n^{n+1}} \right]^{\frac{1}{m+1}} \tag{21}$$

That is, thermodynamic limit of superheat depends only on the parameter n but not on the parameters a, b, c and m of the modified of Berthelot equation of state.

Determination of Equation-of-state Parameters

The parameters of the modified Berthelot equation of state can be determined using any characteristic point on the phase diagram. However,

Table 1 | Parameters of generalized van der Waals and Berthelot equations of state.

| EoS	a $Jkg^{-1}K^{-1}m^3mol^{-1}$	b $10^{-5}\,m^3mol^{-1}$	c $10^{-5}\,m^3mol^{-1}$	m	n
$P = \dfrac{RT}{V-b} - \dfrac{a}{V^n}$	54.3097	1.6433	----	----	1.6945
$P = \dfrac{RT}{V-b} - \dfrac{a}{TV^n}$	271548.44	1.6433	----	----	1.6945
$P = \dfrac{RT}{V-b} - \dfrac{a}{T^m V^n}$	21965.2395	1.6433	----	0.7048	1.6945
$P = \dfrac{RT}{V-b} - \dfrac{a}{\sqrt{T}V^n}$	3840.2749	1.6433	----	----	1.6945
$P = \dfrac{RT}{V-b} - \dfrac{a}{(V+b)^n}$	15.6436	1.1060	----	----	1.8396
$P = \dfrac{RT}{V-b} - \dfrac{a}{(V+c)^n}$	1110	3.3427	-2.8024	----	1.3563

the use of the critical-point parameters in determining the equation of state parameters will improve the accuracy of the equation of state in describing the high-temperature properties of substances. The parameter n for lead is determined through the Eq. (8) using experimental data on the critical compressibility factor.[33-35] The obtained values of n are presented in Table 1. The parameter b for lead is determined through the Eq. (11). The parameters a, c and m are determined through Eqs. (10), (12) and (16), respectively, using experimental data on the critical-point parameters along with values of n. The obtained values of a, b, c and n are presented in Table 1.

Determination of Spinodal

Considering the values of n (Table 1) for lead, the spinodal is determined by Eqs. (18) and (19). The obtained spinodal-parameters are presented in Table 2.
These spinodal-parameters define the stability

boundary of liquid lead in the phase diagram shown in Fig. (2).
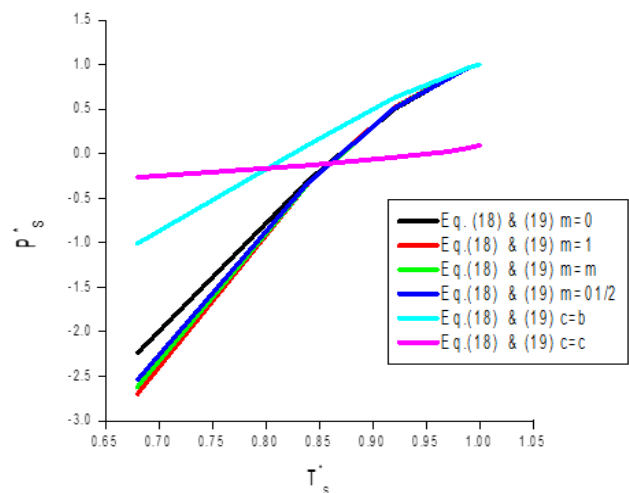
Figure 2 | Spinodal of liquid lead.

Table 2 | Spinodal of liquid lead.

$T_s{}^*$	$P_s{}^*$					
	$m = 0$	$m = 1$	$m = m$	$m = \tfrac{1}{2}$	$c = b$	$c = c$
0.6895	-2.2480	-2.7072	-2.6214	- 2.5445	-1.0157	-2.66E-01
0.8420	-0.3081	-0.3358	-0.3308	-0.3263	0.1047	-1.32E-01
0.9281	0.5010	0.5200	0.5167	0.5136	0.6337	-4.14E-02
0.9736	0.8412	0.8525	0.8505	0.8487	0.8772	2.10E-02
0.9944	0.9703	0.9730	0.9726	0.9721	0.9761	6.44E-02
1	1	1	1	1	1	9.46E-02

Table 3 | Thermodynamic limit of superheat.

Property		$m = 0$	$m = 1$	$m = m$	$m = \frac{1}{2}$	$c = b$	$c = c$
$V^*_{s,0}$	Eq.(20)	0.6289	0.6289	0.6289	0.6289	0.5867	0.7620
$T^*_{s,0}$	Eq.(21)	0.8724	0.9340	0.9230	0.9130	0.8576	0.9190
$V_{s,0}$ 10^{-5} m^3/mol	----	4.0095	4.0095	4.0095	4.0095	3.7404	4.8581
$T^*_{s,0}$ K	----	4362	4670	4615	4565	4288	4595
ΔT K	----	2341	2649	2594	2544	2267	2574

Spinodal of Liquid Lead

The volume at the thermodynamic limit of superheat for lead is determined through Eq. (20) using the values of the parameter n (Table 1). The obtained values are presented in (Table 3). The thermodynamic limit of superheat for lead is determined through Eq. (21) using the values of the parameter n (Table 1). The obtained values are presented in (Table 3). Below the thermodynamic limit of superheat, heterogeneous nucleation prevails. And, above the thermodynamic limit of superheat, homogeneous nucleation will prevail resulting in the explosive boiling of fluids.

Results and Discussion

Several modified van der Waals-Berthelot equations of state have been employed to calculate the spinodal, and thermodynamic limit of superheat of lead. The performance characteristics of these equations of state in evaluating the spinodal, and the thermodynamic limit of superheat of liquid lead have been studied. It has been established that the equation of state with an attractive term of temperature dependence $T^{-1/2}$ more accurately describes the superheating limit of liquid lead. That is, the equation of state with $m = \frac{1}{2}$ gives the thermodynamic limit of superheat of liquid lead of about $0.9T_c$ which agrees with the experimental value for liquid lead.[36] The parameters of the modified van der Waals-Berthelot equations of state are expressed in terms of the critical-point parameters of liquid lead.

It has been established that the four characteristic properties of the fluids, *viz.* the critical pressure, the critical volume, the critical temperature and the Riedel's parameter characterize parameters of the modified van der Waals-Berthelot equations of state. It has been established that liquid lead can be superheated, under rapid heating, up to a temperature 4565 K. That is, liquid lead can be superheated to 2544 K above the normal boiling temperature. This fact is to be taken into account when liquid lead is subjected to rapid heating.

Conclusion

As seen from Table 1, the value of the parameter n is greater than that of the parameter m. That is, the attractive term in the generalized Berthelot equation of state has a stronger dependence on volume than on the temperature. The spinodal (stability boundary on the phase diagram) and the thermodynamic limit of superheat of the liquid lead have been determined using an appropriately modified van der Waals-Berthelot equation of state. The spinodal of liquid lead is presented in Table 2, and is plotted in Figure 2. As seen from Table 2, the liquid lead, under zero pressure, can be superheated to a temperature $0.9130 T_c$. That is, liquid lead can be superheated to 2544 K above the normal boiling temperature. At the thermodynamic limit of superheat, the volume of the liquid lead is 4.0095×10^{-5} m^{3}mol^{-1}. This fact is to be taken into account when liquid lead is subjected to rapid heating.

Conflict of interest

The authors declared no conflict of interest.

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