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A New Four-Parameter Generalized van der Waals Equation of State: Metastable State of Group IV Elements

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Abstract: ***A new four- parameter generalized van der Waals equation of state has been proposed and employed to calculate the spinodal (Metastable State) and the thermodynamic limit of superheat of the of silicon, germanium, lead and tin. It is established that silicon, germanium, tin and lead obey the single parameter law of corresponding states. It is established that the new parameter introduced in the attractive term of the equation of state is a thermodynamic similarity parameter. It has been established that silicon, germanium, tin and lead can be superheated, under rapid heating, up to temperatures 4481K, 7975K, 7161K,and 4333K,respectively. Above these temperatures, silicon, germanium, tin and lead undergo explosive boiling by virtue of homogeneous nucleation. This fact is to be taken into account when silicon, germanium, tin and lead are subjected to rapid heating.***

Keywords: Equation of state, Law of corresponding states, Germanium, Lead,Silicon, Tin,Spinodal, Superheating

1. Introduction

The study of the thermodynamic properties of the silicon, germanium, tin, and lead is of scientific and technological significance. The experimental studies on the thermodynamic properties of the silicon, germanium, tin, lead in the metastable region, encounter severe difficulties. Thus, arises a need for theoretical studies on their thermodynamic properties. In recent years, several studies have been made [1-7] on the thermodynamic properties of silicon, germanium, tin and lead. This fact manifests the relevance of the study of the thermodynamic properties of the silicon, germanium, tin, lead. One of the Statistico-mechanical and thermodynamical approaches to study the thermodynamic properties of substance is the development of equations of state for substances. To improve the accuracy, the known equations of state are generalized [8-20] by modifying the repulsive and attractive terms.

This work is aimed at developing a new equation of state for silicon, germanium, tin and lead in the metastable state. In this work, the known two–parameter generalized van der Waals equation of state is generalized by modifying its repulsive and attractive terms. The performance characteristics of generalized van der Waals equation of state in describing the properties of silicon, germanium, tin and lead in the metastable state are investigated.

2. Generalized van der Waalsequation of state

The known two – parameter generalized van der Waals equation of state does not precisely describe the thermodynamic properties of fluids. This may be attributed to the inaccurate repulsive and attractive terms in the generalized van der Waals equation of state of state. Hence, in this work, this equation is modified by introducing a parameters c in the repulsive term and n in the attractive term. Such a generalized van der Waals equation of state for one mole of substance has the form

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

where P – Pressure, V - Molar volume, T - Temperature, R - Universal gas constant, and a, b c, and n are substance-specific constants.

The vapor-liquid critical point conditions are

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

From Eqs.(1) and (2),we get the critical volume,critical temperature and critical pressure as

$$V_c = N(b-c) \tag{3}$$

Where,

$$N \equiv \frac{n+1}{n-1}$$

$$T_c = \frac{n(N-1)^2 a}{RN^{n+1}(b-c)^{n-1}} \tag{4}$$

$$P_c = \frac{a}{N^{n+1}(b-c)^n} \tag{5}$$

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

$$Z_c \equiv \frac{P_c V_c}{RT_c} = \frac{n^2-1}{4n} \tag{6}$$

The generalized van der Waalsequation of state may be rewritten in terms of the reduced variablesas

$$P_s^* = \frac{N}{V^{*n}}\left[\frac{n\left(V^* - \frac{1}{N}\right)}{V^*} - 1\right] \tag{7}$$

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Where,

$$P^* = P/P_c \ , \ V^* = V/V_c \ , \ T^* = T/T_c$$

The reduced equation of state given by Eq.(7) represents the single-parameter law of corresponding states with the thermodynamic similarity parameter *n*. That is, substances obeying the generalized van der Waalsequation of state, with the same values of parameter *n* are thermodynamically similar. That is, such substances, have similar intermolecular force characteristics.

3. Equation-of-state parameters

The parameters *a*,*b*,*c* and *n* of the generalized van der Waals equation of state are determined through the critical–point parameters. Eq. (6) is a quadratic equation with respect to the parameter *n*. the physically meaningful solution (i.e. n>0) of Eq. (6) is

$$n = 2Z_c + \sqrt{4Z_c^2 + 1} \qquad (8)$$

Eq. (4) gives the parameter *a* of the generalized van der Waalsequation of state as

$$a = \frac{(n+1)^2 RT_c V_c^{n-1}}{4n} \qquad (9)$$

Eqs. (3) gives the parameter *b* of the generalized van der Waalsequation of state as

$$b - c = \left(\frac{n-1}{n+1}\right) V_c \qquad (10)$$

Using Eqs.(8)-(10), the parameters of the generalized van der Waalsequation of state can be determined. Moreover, using the Riedel's parameter along with the critical volume, the values of the parameter *b* and *c* can be determined.

4. Spinodal

The knowledge of the spinodal, a characteristic curve on the phase diagram, is essentialin describing the properties of a substance in the critical and in the metastable states. Fig 1 schemtically depicts [21] the vapour-liquid equilibrium curve (bimodal) and the stability boundary curve (spinodal) of substances.

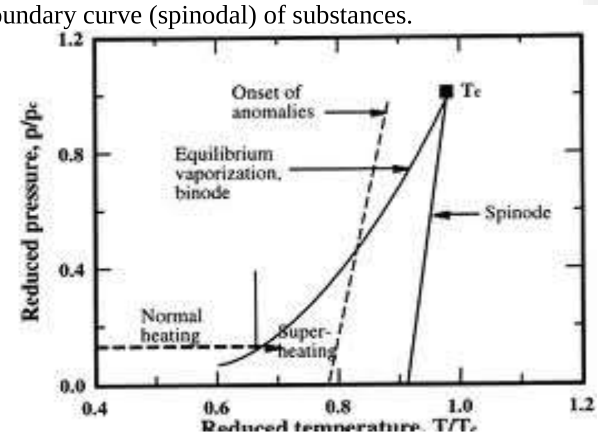


Figure 1

The spinodal defines the thermodynamic Metastable Stateof the phase envelope. The spinodal encloses theregionof unstable states for which the elasticity is negative.For stable states, the 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 [22-32] on the behavior of the superheated metastable fluids. The spinodal is therefore, defined by the condition:

$$-\left(\frac{\partial P}{\partial V}\right)_T = 0 \qquad (11)$$

Applying the condition given by Eq.(11) to Eq.(7), we get the equation of spinodal in *T**, *V** coordinates as

$$T_s^* = \left[\frac{(n^2-1)(NV^*-1)^2}{4NV^{*n+1}}\right] \qquad (12)$$

Substituting Eq. (12) into Eq. (7), we get the equation of spinodal in *P**, *V** coordinates as

$$P_s^* = \frac{N}{V^{*n}}\left[\frac{n\left(V^* - \frac{1}{N}\right)}{V^*} - 1\right] \qquad (13)$$

With a decrease in pressure, the superheat of substances increases. The thermodynamic limit of superheat is attained at

$$P = 0 \qquad (14)$$

Applying the condition given by Eq.(14) to Eq.(7) andusing Eq.(12),we get

$$V_{s,0}^* = \frac{n+1}{n} \qquad (15)$$

Where $V_{s,0}^*$ - The reduced volume of the fluid at the thermodynamic limit of superheat

$$T_{s,0}^* = \frac{1}{4}\left(\frac{n+1}{n}\right)^{n+1} \qquad (16)$$

Where $T_{s,0}^*$ - The thermodynamic limit of superheat

That is, thermodynamic limit of superheat depends only on the parameter *n* but not on the parameters *a*,*b* and *c*of the of generalized van der Waalsequation of state.

5. Determination of Equation-Of-State Parameters

The parameters of the generalized van der Waals equation of state can be determined using any characteristic point on the phase diagram. However, 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*forsilicon, germanium, tin and leadis determined through the Eq. (8) using experimental data [33] on the critical compressibility factor. The obtainzd values of *n* are presented in Table1. The parameter*a*forsilicon, germanium, tin and leadis determined through the Eqs (9)using experimental data on critical-point parameters along with the values of *n*. The parameter *b-c* forsilicon, germanium, tin and leadis determined through the Eq.(10) using experimental data on critical-point parameters along with the values of *n*. The obtained values of*a* and*b-c*are presented in Table 1.

Table 1: Equation-of-state parameters

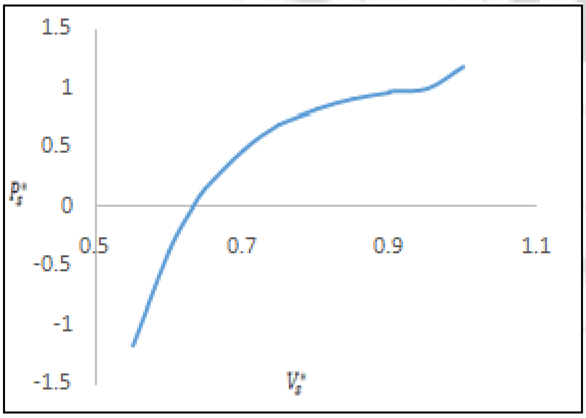
Substance	a 10^5 Pa(m^3.mol^{-1})^n	$b\text{-}c$ 10^{-6}(m^3.mol^{-1})	n
Silicon	4.5476	6.1637	1.7285
Germanium	12.5332	11.7115	1.7195
Tin	13.6081	15.3236	1.7197
Lead	8.7167	16.8070	1.7160

6. Determination of Spinodal

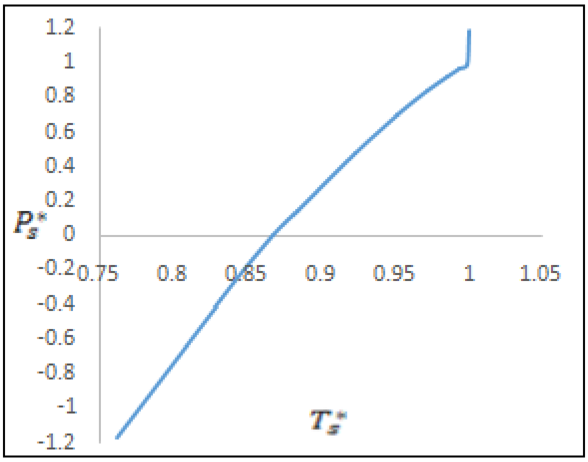
Considering the values of *n* (Table1) forsilicon, germanium, tin and lead, the spinodal is determined by Eqs.(12) and (13).The obtained spinodal-parameters are presented in Tables2-5.These spinodal-parametersdefine the Metastable State ofsilicon, germanium, tin and leadin the phasediagram.

Table 2: Spinodal of Silicon

V_s^*	T_s^*	P_s^*
0.55	0.7619	-1.1641
0.6	0.8320	-0.3679
0.6335	0.8683	0
0.65	0.8846	0.1459
0.7	0.9237	0.4804
0.75	0.9521	0.6969
0.8	0.9722	0.8351
0.85	0.9858	0.9204
0.9	0.9944	0.9701
0.95	0.9988	0.9933
1	1	1.0170



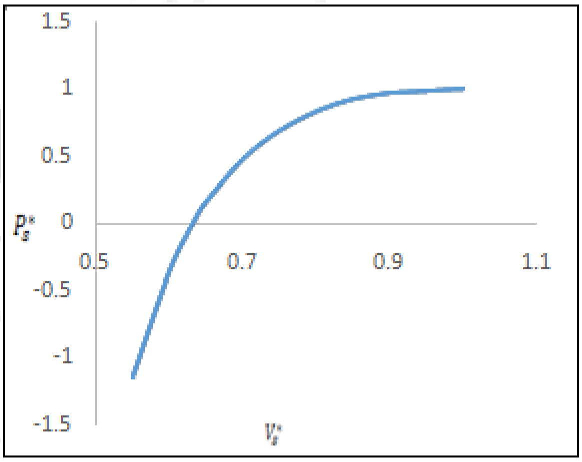
Plot 1.1: Spinodal of Silicon in P-V Coordinates



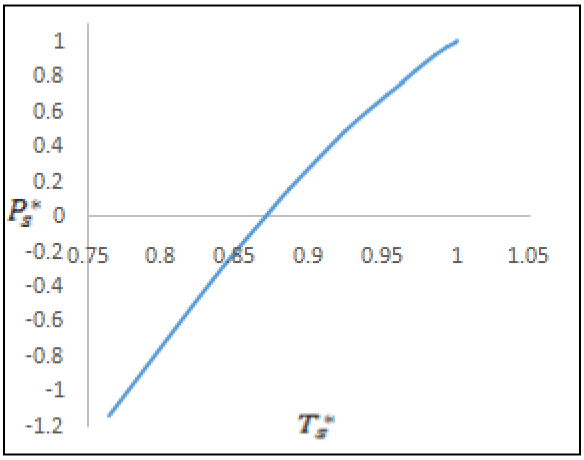
Plot 1.2: Spinodal of Silicon in T-P Coordinates

Table 3: Spinodal of Germanium

V_s^*	T_s^*	P_s^*
0.55	0.7644	-1.1372
0.6	0.8345	-0.3522
0.6323	0.8698	0
0.65	0.8863	0.1555
0.7	0.9247	0.4858
0.75	0.9527	0.6942
0.8	0.9724	0.8367
0.85	0.986	0.9211
0.9	0.9942	0.9696
0.95	0.9987	0.9933
1	1	1



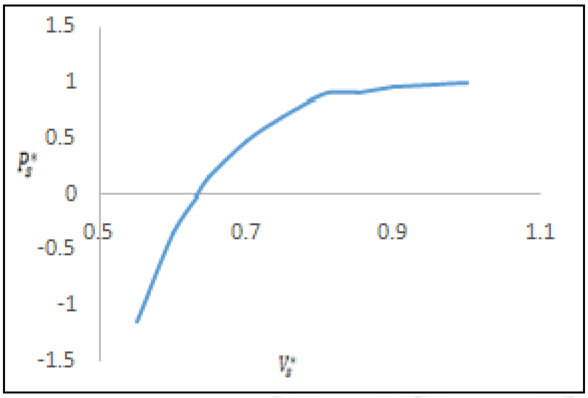
Plot 2.1: Spinodal of Germanium in P-V Coordinates



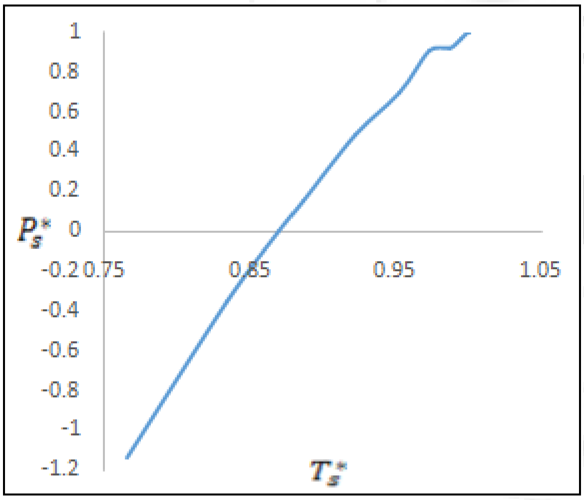
Plot 2.2: Spinodal of Germanium in T-P Coordinates

Table 4: Spinodal of Tin

V_s^*	T_s^*	P_s^*
0.55	0.7656	-1.1382
0.6	0.8344	-0.3527
0.6323	0.8697	0
0.65	0.8863	0.1553
0.7	0.9218	0.4857
0.75	0.9527	0.6999
0.8	0.9725	0.9031
0.85	0.9860	0.9213
0.9	0.9942	0.9697
0.95	0.9987	0.9935
1	1	1



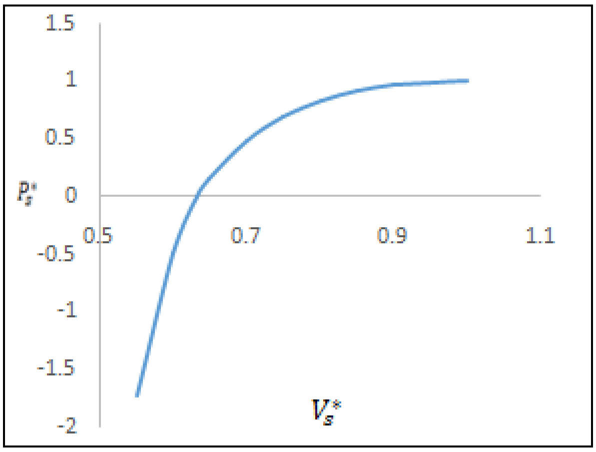
Plot 3.1: Spinodal of Tin in P-V Coordinates



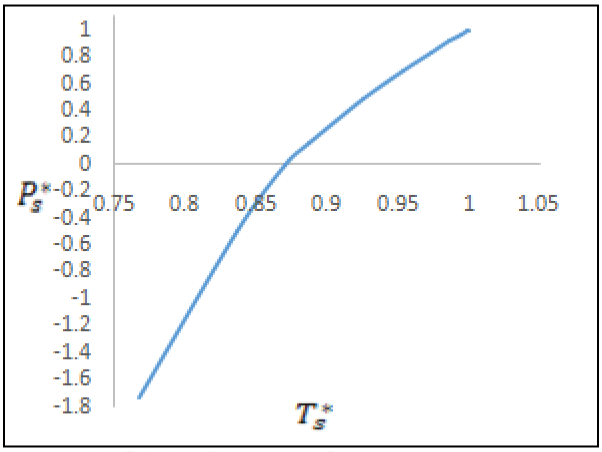
Plot 3.2: Spinodal of Tin in T-P Coordinates

Table 5: Spinodal of Lead

V_s^*	T_s^*	P_s^*
0.55	0.7671	-1.7291
0.6	0.8356	-0.4988
0.6318	0.8701	0
0.65	0.8871	0.1593
0.7	0.9252	0.4879
0.75	0.9529	0.7012
0.8	0.9726	0.8374
0.85	0.9859	0.9215
0.9	0.9943	0.9697
0.95	0.9987	0.9934
1	1	1



Plot 4.1: Spinodal of Lead in P-V Coordinates



Plot 4.2: Spinodal of Lead in T-P Coordinates

7. Determination of thermodynamic limit of superheat

The volume at the thermodynamic limit of superheat forsilicon, germanium, tin and leadaredetermined through Eq.(15) using the values of the parameters *n* (Table1). The obtained values are presented in Table 6. The thermodynamic limit of superheat forsilicon, germanium, tin and lead is determined through Eq.(16) using the values of the parameters *n* (Table1). The obtained values are presented in Table 6.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.

Table 6: Thermodynamic limit of superheat

Substance	$T^*_{s,0}$	$V^*_{s,0}$	$T_{s,0}$ k	$V_{s,0}$ $10^{-5}m^3/mol$
Silicon	0.8683	0.6335	4481	1.4625
Germanium	0.8697	0.6323	7975	2.7989
Tin	0.8697	0.6323	7161	3.6615
Lead	0.8701	0.6318	4333	4.0280

8. Results and Discussion

The four- parameter generalized van der Waalsequation of state has been employed to calculate the spinodal, and thermodynamic limit of superheat ofsilicon, germanium, tin and lead. The performance characteristics of the generalized van der Waals type equation of state in evaluating the spinodal, and the thermodynamic limit of superheat ofsilicon, germanium, tin and leadhave been studied.The parameters of the generalized van der Waalsequation of state are expressed in terms of the critical-point parameters ofsilicon, germanium, tin and lead. Thus, is has been established that the three characteristic properties of the fluids viz., the critical pressure, the critical volume and the critical temperature characterize the generalized van der Waalsequation of state. It has been established thatsilicon, germanium, tin and leadcan be superheated, under rapid heating, up to temperatures 4481K, 7975K, 7161K and 4333K respectively. That is silicon can be superheated to above 943 K above their normal boiling temperatures. germanium can be superheated to above 4819 K above their normal boiling temperatures. tin, can be superheated to above 4302 K above their normal boiling temperatures and lead can be superheated to above 2310 K above their normal boiling temperatures. This fact is to be taken into account whensilicon, germanium, tin and leadare subjected to rapid heating.

9. Conclusion

A new four-parameter generalized van der Waalsequation of state is proposed for describing the high-temperature properties ofsilicon, germanium, tin and lead.Itis established thatsilicon, germanium, tin and leadobey the single parameter law of corresponding states. It is established that the newly introduced parameter *n* is a thermodynamic similarity parameter. The spinodal (Metastable State on the phase diagram) ofsilicon, germanium, tin and leadhas been determined.The thermodynamic limit of superheat ofsilicon, germanium, tin and leadhas been determined.

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