American Journal of Materials Science and Application
2019; 7(3): 60-64
http://www.openscienceonline.com/journal/ajmsa
ISSN: 2381-6074 (Print); ISSN: 2381-6090 (Online)

Thermodynamic Limit of Superheat of Fluids by a Generalized Berthelot Equation of State

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To cite this article
Balasubramanian Ramasamy. Thermodynamic Limit of Superheat of Fluids by a Generalized Berthelot Equation of State. *American Journal of Materials Science and Application.* Vol. 7, No. 3, 2019, pp. 60-64.

Received: May 27, 2019; **Accepted**: August 28, 2019; **Published**: October 23, 2019

Abstract

Superheated metastable states are formed when substances are subjected to rapid heating. At a given temperature and pressure, the free energy of a metastable state is greater than that of the stable state. The thermodynamic limit of superheat, the maximum attainable temperature of superheating under zero pressure, is a characteristic thermodynamic property of substances. The knowledge of the thermodynamic limit of superheat is essential in understanding the behavior of substances in the metastable state. The thermodynamic limit of superheat is marked by the spinodal, a characteristic curve on the phase diagram, of substances. Hence, the study of the thermodynamic limit of superheat of substances is scientifically significant. Moreover, the knowledge of the thermodynamic limit of superheat of substances is required in defining the safety procedures in metallurgical melting, nuclear reactors, cryogenic systems and in the transport of liquefied natural gas. Besides, the superheated liquids are employed in the bubble chambers and in the detectors of neutrons, gamma rays and other charged particles. In this work, the thermodynamic limit of superheat of helium, neon, lithium, sodium, carbon dioxide and nitrous oxide is determined using a generalized Berthelot equation of state. This three- parameter equation differs from the known Berthelot equation of state by the modified expression for molecular pressure. For helium, neon, lithium, sodium, carbon dioxide and nitrous oxide, the parameters of the generalized Berthelot equation of state have been determined through the critical –point parameters. It has also been established that the parameters of the thermodynamic limit of superheat can be used as the corresponding-states parameters.

Keywords

Carbon Dioxide, Corresponding States, Equation of State, Helium, Lithium, Metastable State, Neon, Nitrous Oxide, Sodium, Spinodal, Thermodynamic Limit of Superheat

1. Introduction

Superheated metastable states are formed when substances are subjected to rapid heating [1-8]. At a given temperature and pressure, the free energy of a metastable state is greater than that of the stable state. The thermodynamic limit of superheat, the maximum attainable temperature of superheating under zero pressure, is a characteristic thermodynamic property of substances. The knowledge of the thermodynamic limit of superheat is essential in understanding the behavior of substances in the metastable state. The thermodynamic limit of superheat is marked by the spinodal, a characteristic curve on the phase diagram, of substances. Hence, the study of the thermodynamic limit of superheat of substances is scientifically significant. Moreover, the knowledge of the thermodynamic limit of superheat of substances is required in defining the safety procedures in metallurgical melting, nuclear reactors, cryogenic systems and in the transport of liquefied natural gas. Besides, the superheated liquids are employed in the bubble chambers and in the detectors of neutrons, gamma rays and other charged particles. Due to unfavorable energetic at the liquid-vapor interface, metastable states temporarily exist. According to classical nucleation theory, the metastable states can be kept stable until stochastic fluctuations create critical cluster which then grows spontaneously to make a new phase [9]. However, the metastable states cease to exist when the liquid or vapor is brought to its stability limit i.e spinodal. In this case, phase transition takes place via spinodal decomposition [10] whose mechanism is the homogeneous nucleation [11]. The very short lifetime of systems near the stability limit does not allow the experimental determination of the spinodal and the thermodynamic limit of superheat of substances. Hence, the prediction of the stability limit and thermodynamic limit of superheat from a molecular model of substances acquires significance. The fact that numerous phenomena in industry, meteorology and biology depend on the metastability underscores the technological significance of the study of the thermodynamic limit of superheat of substances.

The present work, based on the generalized Berthelot equation of state, deals with the determination of the parameters of the thermodynamic limit of superheat of helium, neon, lithium, sodium, carbon dioxide and nitrous oxide. The study of the thermodynamic properties of these substances is scientifically and technologically significant. Owing to this fact, in recent years, numerous studies [12-55] have made on the thermodynamic properties of these substances. The choice of these substances for the given study is aimed at evaluating the performance characteristics of the generalized Berthelot equation of state.

2. Generalized Berthelot Equation of State

An improvement of the known Berthelot equation of state, for making it suitable for precise description of the thermodynamic properties of fluids, has been proposed [37] by introducing a third parameter *m* in the expression for molecular pressure. Such a generalized Berthelot equation of state for one mole of substance is

$$P = \frac{RT}{V-b} - \frac{a}{T^m V^2} \tag{1}$$

Where *a, b* and *m* are constants for a given substance, calculated from experimental data. The substance–specific parameter *m* is a measure of intermolecular attractive forces of substances.

The liquid-vapor critical point conditions [56] are

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \tag{2}$$

Application of these conditions to the equation of state given by Eq. (1) produces two equations in the critical volume V_c and the critical temperature T_c Eliminating T_c between them gives

$$V_c = 3b \tag{3}$$

Back substitution in the two equations then gives the critical temperature as

$$T_c = \left(\frac{8a}{27Rb}\right)^{\frac{1}{m+1}} \tag{4}$$

Finally, substitution of *Vc* and *Tc* in Eq. (1) gives the critical pressure as

$$P_c = \left(\frac{aR^m}{27\times 8^m b^{m+2}}\right)^{\frac{1}{m+1}} \tag{5}$$

The critical compressibility factor is then given by

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} \tag{6}$$

Taking into account Eqs. (3)-(6), we may write Eq. (1) in terms of the reduced variables

P*=P/Pc, V*=V/Vc, T*=T/Tc

as

$$P^* = \frac{8T^*}{3V^* - 1} - \frac{3}{T^{*m} V^{*2}} \tag{7}$$

The reduced equation of state given by Eq. (7) represents the single–parameter law of corresponding states with the thermodynamic similarity parameter *m*. That is, substances obeying the generalized Berthelot's equation of state given by Eq. (1), with the same value of parameter *m*, are thermodynamically similar. Such substances have similar intermolecular force characteristics.

The parameters *a, b* and *m* of the generalized Berthelot's equation of state given by Eq. (1) can be determined through the critical-point parameters of substances. From Eqs. (3) and (4), we get

$$a = \frac{9RV_c T_c^{\,m+1}}{8} \tag{8}$$

$$b = \frac{V_c}{3} \tag{9}$$

On the other hand, the slope of the vapor- pressure curve at the critical point gives the Riedel's parameter of substances. Hence, from Eq. (7), we get the parameter *m* correlated to the Riedel's parameter as

$$m = \frac{\alpha - 4}{3} \tag{10}$$

3. Spinodal and Superheating

The knowledge of the spinodal is essential [57] in describing the properties of substances in the critical and in the metastable states with decreased thermodynamic stability. The spinodal defines the thermodynamic stability boundary of the phase envelope. The thermodynamic stability of the phase is defined by the second derivatives of the Gibbs free energy, one of which is the isothermal elasticity – $(\partial P/\partial V)_T$. The spinodal encloses the region of unstable states for which the isothermal elasticity is negative. For stable states, the isothermal elasticity is positive. The spinodal is, therefore, defined by the condition,

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

Application of the condition given by Eq. (11) to Eq. (7) produces one equation of the spinodal in T^*, V^*, coordinates as

$$T_s^* = \left(\frac{\left(3V^* - 1\right)^2}{4V^{*3}}\right)^{\frac{1}{m+1}} \tag{12}$$

Substitution of Eq. (12) into Eq. (7) gives another equation of spinodal as

$$P_s^* = \frac{\left(3V^* - 2\right)}{V^{*3}}\left(\frac{4V^{*3}}{\left(3V^* - 1\right)^2}\right)^{\frac{m}{m+1}} \tag{13}$$

At zero pressure P^*=0, Eq. (13) gives the reduced volume of the superheated liquid as

$$V_{s,0}^* = \frac{2}{3} \tag{14}$$

From Eqs. (12) and (14), we get the reduced thermodynamic limit of superheat of the liquid at zero pressure as

$$T_{s,0}^* = \left(\frac{27}{32}\right)^{\frac{1}{m+1}} \tag{15}$$

As a characteristic parameter, the thermodynamic limit of superheat at zero pressure, given by Eq. (15), is a useful quantity in the study of fluids as it represents the largest possible difference between the attainable superheat of the liquids and the boiling temperature marked by the binodal on the phase diagram.

Moreover, differentiation of Eq. (7), with Eqs. (14) and (15) taken into account, gives the slope of the spinodal at zero pressure as

$$\left(\frac{dP_s^*}{dT_s^*}\right)_{P^*=0} = 8(m+1) \tag{16}$$

As seen, $\left(\frac{dP_s^*}{dT_s^*}\right)_{P^*=0}$ is also a characteristic parameter of substances as it is determined by the thermodynamic similarity parameter m.

4. Calculations and Analysis

The parameters *a, b* and *m* of the generalized Berthelot equation of state are determined through experimental data on critical-point parameters [55, 58] and on the acentric factor [58] for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide. In these calculations, Eqs. (8)-(10) are employed. The obtained values of the parameters *a, b* and *m* are presented in Table 1.

Table 1. *The parameters of the generalized Berthelot equation of state.*

Substance	*A* $Nm^4K^m/mole^2$	*B* $10^{-5} m^3/mole$	*m*
Helium	0.0029	1.9100	0.0254
Neon	0.1221	1.3900	0.5148
Lithium	13074.1130	10.9900	0.9087
Sodium	74.7840	3.8670	0.4187
Carbon dioxide	342.5360	15.60	0.9707
Nitrous oxide	0.04020	3.233	0.8656

For helium, neon, lithium, sodium, carbon dioxide and nitrous oxide, the parameters of the thermodynamic limit of superheat at zero pressure are determined by Eqs. (14) and (15) with the values the parameter *m* presented in Table 1. The obtained values of the parameters of the thermodynamic limit of superheat at zero pressure for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide are presented in Table 2.

Table 2. *The parameters of the thermodynamic limit of superheat of substances.*

Substance	$T^*_{s,0}$	$V^*_{s,0}$	$\left(\frac{dP_s^*}{dT_s^*}\right)_{P^*=0}$	$T_{s,0}$	$V_{s,0}$ 10-5 m^3/mole	$\left(\frac{dP_s}{dT_s}\right)_{P=0}$ kPa/K
Helium	0.6667	0.8473	8.2032	4.4060	3.8200	359.6788
Neon	0.8939	0.6667	12.1184	39.6892	2.7800	724.1017
Lithium	0.9148	0.6667	15.2696	2713.2968	21.9800	112.1641
Sodium	0.8871	0.6667	11.3496	2282.5083	7.7330	156.4330
Carbon dioxide	0.9174	0.6667	15.7656	279.07308	31.2130	382.8159
Nitrous oxide	0.9130	0.6667	14.9248	282.6374	6.4670	349.5808

Our calculations show that helium, neon, lithium, sodium, carbon dioxide and nitrous oxide can be superheated, at zero pressure, up to temperatures close to the critical temperatures i.e. about 0.9*Tc*. For helium, neon, lithium, sodium, carbon dioxide and nitrous oxide, the value of the slope of the spinodal at zero pressure is determined by Eq. (16) with the values the parameter *m* presented in Table 1. The obtained values of the slope of the spinodal at zero pressure for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide are presented in Table 2. Moreover, using the values of the critical-point parameters, the absolute values of the parameters, and are determined. The obtained values for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide are presented in Table 2.

5. Conclusions

For helium, neon, lithium, sodium, carbon dioxide and nitrous oxide, the parameters of the thermodynamic limit of superheat at zero pressure have been determined by the generalized Berthelot equation of state. It has been established that the parameters of the thermodynamic limit of superheat at zero pressure can be used as thermodynamic similarity parameters for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide. It is found that various substances, depending upon their nature, are superheated to various temperatures. For the studied substances, the reduced thermodynamic limit of superheat varies from 0.7 to 0.9. Beyond the respective temperature limit, the substances undergo explosive boiling due to heterogeneous nucleation. This fact is to be considered in the design of technological applications in which these substances are subjected to rapid heating. Moreover, the temperature derivative of pressure along the spinodal, under zero pressure, has been determined for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide. These values vary from 112kPa/K to 383kPa/K. Thus, this work has determined the characteristic thermodynamic properties such as the thermodynamic limit of superheat and the temperature derivative of pressure along the spinodal, under zero pressure for helium, neon, lithium, sodium, carbon dioxide and nitrous oxide.

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