

# An empirical extension for a generalized cubic equation of state, applied to a pure substance with small molecules



F. de J. Guevara-Rodríguez<sup>a,b,\*</sup>, Ascención Romero-Martínez<sup>a,b,c</sup>

<sup>a</sup> Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México, Distrito Federal, México

<sup>b</sup> Programa de Ingeniería Molecular, México

<sup>c</sup> Área de investigación en Termofísica, México

## ARTICLE INFO

### Article history:

Received 26 October 2012

Received in revised form 11 March 2013

Accepted 12 March 2013

Available online 21 March 2013

### Keywords:

Non-cubic equation of state

Solid phase

Triple point

Phase transition

Pure substance

## ABSTRACT

An equation of state to describe the complete phase diagram of a pure substance is developed. The equation of state is constructed by using a generic cubic equation plus the term  $-fT/(v-e)^{10}$ . This term (where  $f > 0$  and  $e$  are adjustable parameters) is the attractive contribution of the solid phase. It has a volume short-range contribution, and extends the traditional use of a cubic equation, incorporating the thermodynamics description of the solid phase, which allows to represent the experimental triple point, the solid–liquid, and the solid–vapor phase transitions, together with the traditional description of the liquid–vapor transition. For the solid–liquid phase coexistence at any temperature, molar volume predictions of the solid phase define a curve which never connects to its corresponding liquid phase curve. This feature is in agreement with experimental evidences that seem to not accept the existence of a solid–liquid critical point. Finally, calculations for the complete phase diagram for carbon dioxide and argon were carried out in order to show the capabilities and features of the equation of state, and these results were also compared with other predictions from the literature.

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## 1. Introduction

Mechanical equation of state (EOS) has been used to describe thermodynamic properties of pure substances and mixtures. In particular, a cubic EOS predicts quite well the liquid–vapor, and the liquid–liquid phase transition [1–19]. However, to describe the solid phase of a substance with any of the cubic EOS is a complicated task. In the open literature, there are some methods to tackle the problem of representing the solid phase. As an example, cubic EOS has been used for some particular mixtures, where the solid phase is treated as a pure compound [20]. In other example, a cubic EOS has been used to describe the thermodynamic properties of a “mixture” of molecular clusters of a simple substance [21,22]. In this case, biggest molecular clusters are considered part of the solid phase [23], which coexists with the remaining part of the fluid.

In the literature there are also reported some equations of state, which were developed to predict the solid phase, and all of them are non-cubic EOS. For example, Yokozeki [24,25] modified the repulsive part of the van der Waals equation introducing a second discontinuity along the solid–liquid phase transition. In this way, the discontinuity avoids a critical point on the melting curve [24].

This EOS was used to predict the solid phase of some substances, and is a very simple analytical equation, but violates some physical restrictions due to the discontinuity [26].

A second example is the non-cubic EOS developed by Lee et al. [27]. They used the extended Veytsman statistics and a lattice fluid model, and the results with their equation are in agreement with experimental data for fluid phases but underestimate the solid phase density and the triple point temperature.

Perhaps, Kan's work was the first effort to develop a unified EOS, which is able to represent the different phase equilibria along the three most known states of matter solid, liquid, and vapor of argon [28]. In his work, the pressure is approached with some terms of the Virial expansion. Thus, the first three terms correspond to a cubic EOS, which is modified by the fourth term of order 9. In this way, the results with his non-cubic EOS are in agreement with experimental data of argon.

Another effort on this topic was the work from Wenzel and Schmidt [29] who developed their EOS taking as starting point the Redlich–Kwong equation, which is modified with the term  $cT^\xi/(v-0.97b)^6$ , where  $b$ ,  $c$ , and  $\xi$  are the parameters,  $v$  and  $T$  are the molar volume and the temperature, respectively. Last term is the attractive contribution of the solid phase, has a volume short-range, and is negligible in the liquid–vapor phase transition region. However, the resulting melting curve shows a critical point as an undesirable feature.

In this work, an EOS to represent the complete phase diagram of a pure substance is proposed. The EOS is basically a general cubic

\* Corresponding author. Tel.: +52 55 9175 8176.

E-mail address: [fguevara@imp.mx](mailto:fguevara@imp.mx) (F. de J. Guevara-Rodríguez).

equation, which was reported elsewhere [19], and it is modified by adding the term  $-fT/(v-e)^{10}$ . The last term is the attractive contribution of the solid phase. The main features of the resulting EOS is described in Section 2, and the method to determine its parameters is described in Section 3. Furthermore, the capabilities of the EOS are exhibited through the calculation of the phase diagram for argon and carbon dioxide, and its results are also shown in Section 3. Finally, the results are also compared with the results obtained with other equations from the literature.

## 2. Equation of state

The state of a fluid is defined by its temperature ( $T$ ), molar volume ( $v$ ), and pressure ( $P$ ). These thermodynamic variables are not independent because they are related through mechanical EOS. The EOS, which is proposed, has the following structure

$$P(T, v) = \frac{RT}{v-b} - \frac{A(T)}{(v-c)(v-d)} - \frac{fT}{(v-e)^{10}}, \quad (1)$$

with

$$A(T) = aT(e^{\varepsilon/RT} - 1), \quad (2)$$

where  $R$  is the gas constant, and  $\{a, b, c, d, e, f, \varepsilon\}$  is the set of parameters, which depends on the fluid. The methodology to evaluate the parameters will be described later.

If  $f=0$ , Eq. (1) becomes a cubic EOS. However, in general, two cases have to be considered:  $f=0$  and  $f>0$  together with  $b>e$ . For the case when  $f>0$ , the last term of Eq. (1) has a volume short-range nature, which is related to the attractive contribution of the solid phase, and modifies the liquid–vapor coexistence obtained by the cubic EOS. Perhaps, a possible microscopic mechanism, which could explain the origin of the above attractive term, is the conjecture of DeBenedetti et al. [30] who argue that an effective pair potential, attractive at the nearest distances and repulsive at a second nearest distance, induces a liquid phase where its structure collapses into a solid phase at high pressures, and therefore, the solid–liquid coexistence is established.

The schematic representation of the pressure–volume diagram, which could be obtained using Eq. (1), is illustrated in Fig. 1. In this figure, outer solid curve is the phase coexistence diagram and the inner dashed curve is the spinodal curve. Eq. (1) has two particular points which fulfill

$$P(T_c, v_c) = P_c; \quad (3a)$$

$$\left(\frac{\partial P}{\partial v}\right)_c = 0; \quad (3b)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_c = 0. \quad (3c)$$

The first of them, which is labeled as  $C_1$  in Fig. 1, corresponds to the critical point of the liquid–vapor phase coexistence. In this case, the last term in the Eq. (1) is negligible and the critical point is determined practically with the cubic EOS. Moreover, the phase diagram for the liquid–vapor coexistence, which is obtained with Eq. (1), can be practically approached with the cubic EOS.

On the other hand, the second point, which is labeled as  $C_2$  in Fig. 1, is not a critical point of the fluid, it has a negative pressure, and it could be used to locate the melting region and the triple point.

In the literature, there are not reported experimental evidences of a critical point for the solid–liquid phase coexistence. However, in the work of Elenius and Dzugutov [31], theoretical evidence of a solid–liquid critical point is suggested through the molecular-dynamics simulation of a monoatomic system. In their work, a liquid–crystal phase coexists with the liquid phase [31]. Thus, the

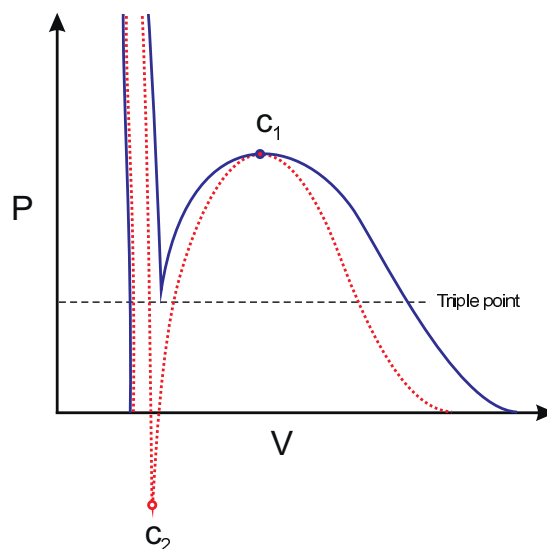


Fig. 1. Schematic representation of a typical phase coexistence diagram (solid curve), which can be constructed using Eq. (1). The dashed curve corresponds to the spinodal curve.

transformation of the liquid phase into the solid phase could be continuous, and the melting curve must finish at the critical point. In this work, Eq. (1) does not have a critical point for the solid–liquid coexistence, and this is illustrated in Fig. 1 with an indefinite solid branch, which never connects its corresponding liquid branch. Moreover, for a high temperature, Eq. (1) can be rewritten as

$$\lim_{T \rightarrow \infty} \frac{P}{T} = \frac{R}{v-b} - \frac{f}{(v-e)^{10}}. \quad (4)$$

Eq. (4) could describe a solid–liquid coexistence for a proper set of parameters, and therefore, the critical point does not exist. On the other hand, the behavior of any fluid at high temperatures could be approached with a hard sphere model. Thus, the solid transition of the ideal fluid is a first order transition, and its solid–liquid critical point does not exist [32]. In this work, the solid–liquid critical point is not a feature of Eq. (1). Moreover, we cannot conclude anything about the existence of the solid–liquid critical point for a real fluid. Contrary to our Eq. (1), solid–liquid critical point is a consequence for other equations from literature [33,27,28,21,29].

Finally, the method to determine the parameters of the EOS will be described in the next section.

## 3. Method

All parameters from Eq. (1) are strongly related to the specific substance under study, and all of them are exclusive for the substance. In this section the method to determine the parameters is presented. Parameters of the cubic EOS are firstly determined. This step is the starting point of the method. The procedure was reported elsewhere [19], but here, it is also presented in Section 3.1. After that, the parameters  $f$  and  $e$ , which are related to the attractive contribution of the solid phase in Eq. (1), are determined using the experimental triple point data of the substance. This is the second step, and its details are presented in Section 3.2. Finally, the calculations for the phase diagram of argon and carbon dioxide are presented in Section 3.3, and both cases are used to show the features of our EOS. The results, which are derived with our EOS,

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