



# A new equation of state for gaseous, liquid, and supercritical fluids



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## ABSTRACT

In the present study, a new equation of state (EOS) was derived by using the thermodynamic equation of state and the intermolecular potential (3, 9, 12). It was shown that the EOS is applicable in low and high ranges of temperature, pressure and density for gaseous, liquid and supercritical fluids and even in liquid–gas phase transition region. The new EOS is applicable for a variety of fluids such as polar, nonpolar, rare gases, short-chain and long-chain hydrocarbon fluids. The absolute percent deviation of the calculated density for gaseous, liquid and supercritical fluids is very low. The common bulk modulus point and the common compression point regularities were predicted by the new EOS. The new EOS was compared with some equations of state which had been derived similarly. It is shown that the repulsive potential used in the EOS derivation is effective in predicting correct fluid properties.

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## 1. Introduction

The structure and properties of substances depend on intermolecular forces. Many studies for the careful formulation of the relationship between the bulk properties of substance and intermolecular forces have been done [1–5]. Such formulation is the ultimate goal of the molecular theory of substances. By developing such theories, all the bulk properties of substance can be evaluated just by knowing intermolecular forces [6–9].

Clearly, a close relationship between the macroscopic properties of fluids and the intermolecular forces can be established by the equation of state (EOS). Parsafar and Mason provided a general EOS for compressed solids using a universal binding energy [10]. The linear isotherm regularity, LIR, which is applicable for dense and supercritical fluids, was obtained based on a lattice model with Lennard-Jones potential (6, 12) [11] and then extended to mixtures [12]. The LIR predicts a linear behavior of  $(Z - 1)v^2$  isotherms versus  $\rho^2$  for  $\rho\rho_B$  and  $T(2T_B)$ , where  $\rho = 1/v$  and  $T_B$  are the molar density and Boyle temperature, respectively. Goharshadi et al. derived an EOS (GMA) by a similar method as the LIR, based on the average potential (9, 12) [13]. The GMA EOS predicts the linear behavior of  $(2Z - 1)v^3$  isotherms versus  $\rho$  in  $T(T_C)$  and  $\rho\rho_C$  where  $T_C$  and  $\rho_C$  are the critical temperature and density, respectively. Ghatee and Bahadori [14] provided an EOS for liquid metals using the potential (3, 6) which predicts that the  $(Z - 1)v^2$  isotherms versus  $1/\rho$  are

linear. Baniasadi and Ghader (BGH) [15] obtained an EOS using the potential (3, 6, 9) that is applicable for the entire range of liquid and gas in high pressures and densities. Parsafar et al. [16] provided an EOS (PSP) using the potential (3, 6, 12). This equation holds for liquid metals, short-chain hydrocarbon, polar, nonpolar, and hydrogen-bonding fluids. In addition, the behavior of metallic, covalent and ionic solids is justified by this equation. The application range variety related to the equations of state and obtained by the potentials (6, 12), (3, 6, 9) and (3, 6, 12) refers to the role of the potential type in the applicability of the EOS. The derivation method of the mentioned equations of state was almost equal; however, there are many equations of state that used the model potential functions for the prediction of the fluid properties in different temperatures and pressures like PC-SAFT and SAFT-VR descriptions [17–20].

In this work a new interaction potential, (3, 9, 12), was considered for fluids that had not been used before. The repulsion, the attraction and the long range interaction like polar–polar interactions are included in the potential function. The derived EOS parameters have the molecular basis and the fluid properties can be described in terms of the molecular interactions.

This paper has been organized as follows: in part 2, an EOS with three temperature dependent parameters is derived by employing the thermodynamic equation of state and the interaction potential (3, 9, 12). Accordingly, the temperature dependencies of the new EOS parameters are obtained. In part 3, the applicability of the EOS for a variety of fluids in different temperatures and densities, and also in the liquid–gas transition region is investigated. In addition,

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the EOS ability predicting the density of fluid is determined and the common bulk modulus point and the common compression point regularities are investigated by the new EOS in this part. In part 4, the new EOS is compared with GMA, BGH and PSP equations of state, and the role of interaction potential is discussed. Finally, the conclusion is presented in part 5.

## 2. Equation of state derivation

Equations of state are the key relations for the calculating the thermodynamic properties of substances. The properties of substances are related to their intermolecular potentials. Therefore, a close relationship between equations of state and the intermolecular forces is expected. As mentioned before, several equations of state were obtained, based on the intermolecular potential while each having its own advantages.

Clearly, the attractive range increases with adding  $r^{-3}$  term in the functional form of the potential. It was shown that the application range of the extracted equations of state increased by using this form of potential in terms of fluid variety, temperature and density [15,16]. So, in the present work, the potential (3, 9, 12) is used for deriving EOS and comparing it with any similar EOSes. The functional form of the potential (3, 9, 12) with temperature-dependent coefficients is:

$$U = \frac{N}{2} z \left( \frac{C_{12}(T)}{r^{12}} + \frac{C_9(T)}{r^9} + \frac{C_3(T)}{r^3} \right) \quad (1)$$

where,  $N$  is number of molecules,  $z$  is density independent coordination number,  $r$  is distance between two molecules, and  $C_i$  is temperature-dependent coefficient of the potential function. The term  $r^{-3}$  in Eq. (1) relates to the long-range interactions and assigned to the polar–polar interactions. The terms  $r^{-9}$  and  $r^{-12}$  attribute to attraction and repulsion interactions, respectively.

Replacing  $r = kv^{1/3}$  into Eq. (1) and rearranging the result, yield:

$$\frac{U}{N} = \left( \frac{C'_{12}(T)}{v^4} + \frac{C'_9(T)}{v^3} + \frac{C'_3(T)}{v} \right) \quad (2)$$

where,  $C'_3(T)$ ,  $C'_9(T)$  and  $C'_{12}(T)$  are new temperature-dependent coefficients of the potential function. Here, we assumed that the temperature dependencies of  $C'_i$  coefficients are quadratic as:

$$C'_{12}(T) = A''_1 + A''_2 T + A''_3 T^2 \quad (3)$$

$$C'_9(T) = B''_1 + B''_2 T + B''_3 T^2 \quad (4)$$

$$C'_3(T) = C''_1 + C''_2 T + C''_3 T^2 \quad (5)$$

where  $A''_i$ ,  $B''_i$ , and  $C''_i$  are constant values that depend on the system. Replacing Eqs. (3)–(5) into Eq. (2), gives:

$$\frac{U}{N} = \left( \frac{A''_1 + A''_2 T + A''_3 T^2}{v^4} + \frac{B''_1 + B''_2 T + B''_3 T^2}{v^3} + \frac{C''_1 + C''_2 T + C''_3 T^2}{v} \right) \quad (6)$$

Using Eq. (6), the internal pressure,  $P_i$  can be calculated by,

$$P_i = \left( \frac{\partial \left( \frac{U}{N} \right)}{\partial v} \right)_T \quad (7)$$

The following thermodynamic equation of state connects the internal pressure to the pressure:

$$P = T \left( \frac{\partial P}{\partial T} \right)_\rho - P_i \quad (8)$$

where  $T(\partial P/\partial T)_\rho$  is thermal pressure.

Then, the EOS can be obtained by replacing Eq. (6) into (7) and gaining Eq. (8). Making some rearrangements gives:

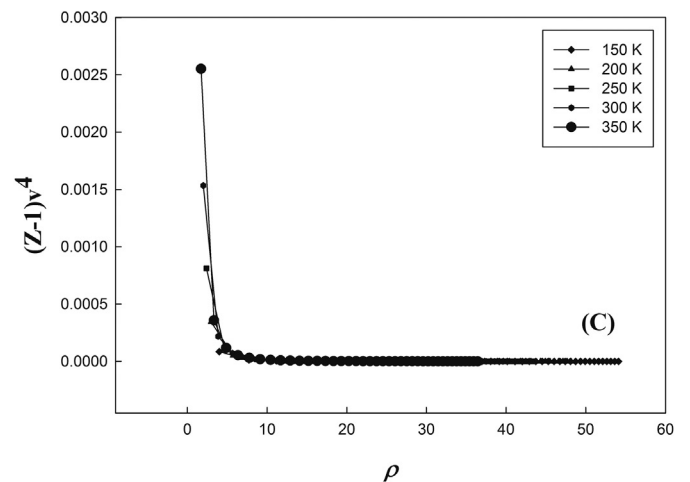
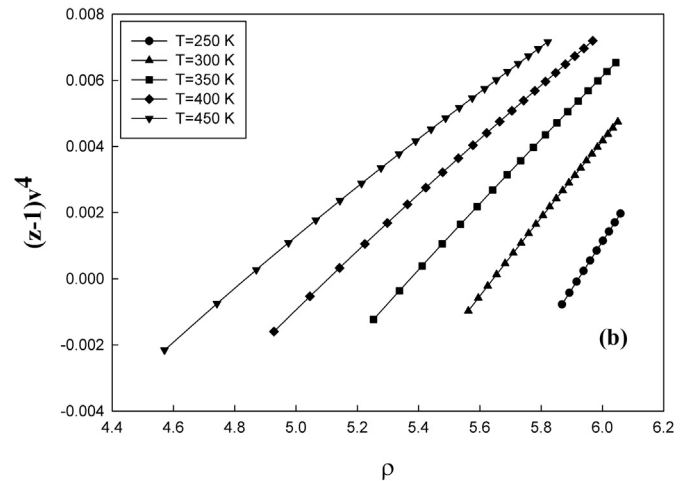
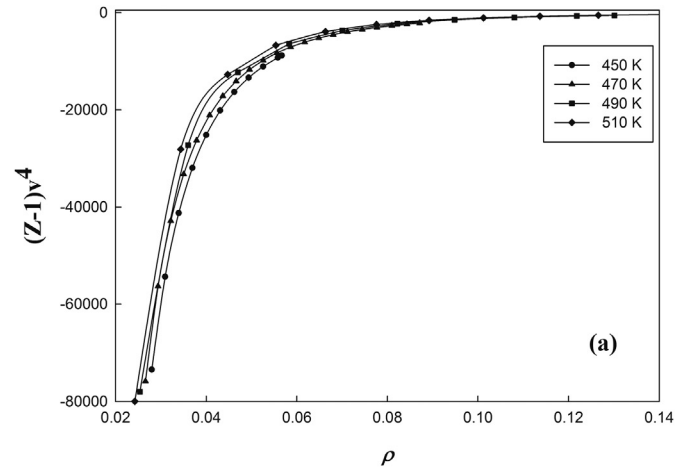


Fig. 1. The isotherms of  $(Z - 1)v^4$  vs  $\rho$  for  $C_9H_{20}$  in a) gaseous, b) liquid, and c) supercritical states. The symbols show the experimental values and the lines show the fitted values with the new EOS.

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