

# A semi-empirical equation of state of saturated liquids



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## ABSTRACT

A new semi-empirical equation of state based on a modified application of the theorem of corresponding states has been presented for saturated liquids. An optimization algorithm was used to obtain unknown parameters of this equation by fitting them with the experimental data. There is an acceptable agreement between the predicted values of reduced compressive factor of saturated liquids and the experimental data for 79% of 231 cases.

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## 1. Introduction

In thermodynamics, an equation of state is a relation between state variables. This equation describes the state of matter under a given set of physical conditions. This fundamental equation provides a mathematical relationship among temperature, pressure and molar volume. Equations of state are useful in describing the properties of pure gases and liquids or mixtures of them. Until now, much attention has been directed to develop generalized relations for predicting the thermodynamic properties of gaseous state. Nevertheless, the thermodynamic properties of liquids have received little attention, because of failure of the theorem of corresponding states to establish an accurate relation for liquid properties [1]. According to this theorem, all fluids at a same reduced temperature and reduced pressure, have approximately a same compressibility factor [2,3]. Modifying this theorem can makes them applicable to predict the properties of liquids, accurately.

Some of the properties of saturated liquids have been listed in many tables in references [4]. These values can be extracted using a suitable table look-up computer program. When the volume of computations is enormous, a simple but accurate formula would be useful. In these conditions, which large numbers of values are required, it is common to compute each value using an appropriate formula. This formula can be utilized to compute the related property in any operating conditions.

The variation [5] and perturbation [6] theories are mathematical approaches to expand the thermodynamic properties of fluids. The basic idea behind these theories is that, at high temperatures, fluids behave like assembled hard-spheres with only the repulsive forces between the molecules. These theories have been successful in accurately predicting of the liquid properties, but are not applicable for engineering calculations. Because, these theories have complex mathematical relations, therefore, require numerical calculations and excessive use of computer time.

In the present article, a novel equation of state is presented for saturated liquids. This equation is based on a modified application of the theorem of corresponding states and fitting with the experimental data. Critical temperature ( $T_r$ ), critical pressure ( $P_r$ ), and critical liquid molar density ( $v_r^l$ ) are required to predict reduced compressibility factor of saturated liquid ( $z_r^{\text{sat}}$ ) using this equation. Like all of the applications of this theorem, the obtained equation is not correct, exactly. Nevertheless, deviations of predicted values from the experimental data are small enough to warrant its utilization in many of process problems.

## 2. Development of the equation

### 2.1. Theory

The simplest and best-known equation of state for ideal gases is given as  $Pv = RT$ . The deviation from ideal-gas behavior can be properly accounted using the compressibility factor (the ratio of the molar volume of a gas to the molar volume of an ideal gas at the same temperature and pressure),  $z$ , which is defined as  $z = Pv/RT$ . This factor is a function of reduced temperature and reduced pressure. Therefore,  $z$  is approximately the same for all gases at the

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Nomenclature	
$B$	Second virial coefficient
$FB$	Fractional bias, which is defined as $FB = 2 \times \frac{Z_r^{1,sat} \text{ Experimental} - Z_r^{1,sat} \text{ Model}}{Z_r^{1,sat} \text{ Experimental} + Z_r^{1,sat} \text{ Model}}$
$NMSE$	Normalized mean square error, which is defined as $NMSE = \frac{\sum (Z_r^{1,sat} \text{ Experimental} - Z_r^{1,sat} \text{ Model})^2}{Z_r^{1,sat} \text{ Experimental} \times Z_r^{1,sat} \text{ Model}}$
$NRMSE$	Normalized mean square error, which is defined as $NRMSE = \sqrt{\sum (Z_r^{1,sat} \text{ Experimental} - Z_r^{1,sat} \text{ Model})^2}$
$P$	Pressure (Pa)
$P_c$	Critical pressure (Pa)
$P_r$	Reduced pressure, define as $P_r = \frac{P}{P_c}$
$P_r^{sat}$	Reduced saturated pressure
$R$	Universal Gas Constant ( $\text{Pa m}^3 \text{ mol}^{-1} \text{ K}$ )
$R^2$	The coefficient of determination, which is defined as $R^2 = 1 - \frac{\sum (Z_r^{1,sat} \text{ Experimental} - Z_r^{1,sat} \text{ Model})^2}{\sum (Z_r^{1,sat} \text{ Experimental} - Z_r^{1,sat} \text{ Experimental})^2}$
$T$	Temperature (K)
$T_c$	Critical temperature (K)
$T_r$	Reduced temperature, define as $T_r = \frac{T}{T_c}$
$v$	Molar volume ( $\text{m}^3 \text{ mole}^{-1}$ )
$v_c$	Critical molar volume ( $\text{m}^3 \text{ mole}^{-1}$ )
$v^L$	Liquid molar volume of saturated liquids ( $\text{m}^3 \text{ mole}^{-1}$ )
$v_r^L$	Reduced molar volume of saturated liquids, define as $v_r = \frac{v^L}{v_c} v_r = \frac{v^L}{v_c}$
$Z$	Compressibility factor
$z_c$	Critical compressibility factor
$Z_r$	Reduced compressibility factor of gases
$Z_r^{1,sat}$	Reduced compressibility factor of saturated liquid

same reduced temperature and reduced pressure. Dividing  $z$  to critical compressibility factor ( $z_c$ ), which is a property of substance as  $z_c = P_c v_c / RT_c$ , yields reduced compressibility factor ( $z_r$ ) as  $z_r = z / z_c = P_r v_r / T_r$ . Therefore, this factor is a property of substance and also is a function of conditions. In the other word,  $z_r$  accounts mainly two things, molecular structure and intermolecular attractive forces. The Virial equation of state of gases has additional terms beyond that for an ideal gas, which account for these interactions between the molecules. This equation derives from a perturbative treatment of statistical mechanics. Perturbation theory includes mathematical methods to find an approximate solution for a problem [7]. This theory breaks the problem into solvable and perturbation parts. Using this theory, the follow equation can be presented for calculating  $z_r$ :

$$z_r = 1 + \frac{B}{v_r} + \frac{C}{v_r^2} + \frac{D}{v_r^3} + \dots \quad (1)$$

where  $B, C, D$  and also other numerators are functions of  $T_r$ . An approximate is obtained by shorten this series, usually by keeping only the first two terms (i.e.,  $z_r = 1 + B/v_r$ ).

A gas in the extremely dilute state, i.e., in the low pressure and high temperature conditions, where the volume is so large, i.e., the molecules can be regarded as points, consists of small moving molecules, is an ideal gas. On the other side, saturated liquids can be regarded as compressed gases at low temperature. Thus, this idea is conceived that there is no essential difference between the saturated liquid and the gaseous state. The most important

difference between these two states of matter is definition of the pressure. The motion of the molecules determines the pressure of the gases. This quantity is changed when the density and also temperature were changed. Saturation pressure ( $P^{sat}$ ) is the pressure for a corresponding saturation temperature at which a liquid boils into its vapor phase. From the other point of view, the saturated pressure is the pressure on the gas–liquid interfaces, which opposes to the vaporization of the saturated liquid. Increasing of the liquid temperature increases the motion of saturated liquid molecules. This motion of the molecules determines the required pressure to prevent the vaporization of this liquid. Therefore, the saturated pressure of liquids is corresponds to the pressure of gases. Therefore, the compressibility factor of saturated liquids ( $z^{1,sat}$ ) can be presented as  $z^{1,sat} = \frac{P^{sat} v_r^L}{RT}$ . Dividing  $z^{1,sat}$  to  $z_c$  yields reduced compressibility factor of saturated liquid ( $z_r^{1,sat}$ ) as  $z_r^{1,sat} = \frac{z^{1,sat}}{z_c} = \frac{P^{sat} v_r^L}{T_r P_c v_c}$ . This quantity can be calculated using the experimental data of  $T_r, P_r^{sat}$  and  $v_r^L$  for each saturated liquid.

Intermolecular bonds held molecules of liquids together. When a liquid reaches its saturated condition, the cohesive force that binds the molecules closely together is broken, and the liquid starts to change to its gaseous state. Therefore, in the saturated liquids this force is limited but not removed. This is the major cause of inapplicability of the Virial equation in the saturated liquid state. Since these intermolecular bonds are a property of the substance, a function of the critical compressibility factor,  $f(z_c)$ , which is a property of substance, can be used to modify the Virial equation for utilizing in the saturated liquid state as below:

$$z_r^{1,sat} = f(z_c) \times \left( 1 + \frac{g(z_c, T_r)}{v_r^L} \right) \quad (2)$$

A similar modification is done on the equation of state of gaseous phase by Watson [1]. As previously mentioned, there is a direct relation between Virial coefficient,  $B$ , and intermolecular potential, which is a function of temperature. Hence, a universal function of reduced temperature has been presented for  $B = g(T_r)$  in the gaseous state [8]. Nevertheless, in the saturated liquids,  $g(z_c, T_r)$  is a function of critical compressibility factor and reduced temperature. Because, this parameter should also contains the explained effects of intermolecular bonds in saturated liquids.

## 2.2. Obtaining equation parameters

Obtaining two unknown functions of Eq. (2), i.e.,  $f(z_c)$  and  $g(z_c, T_r)$ , is necessary to estimate the thermodynamically properties of saturated liquid. These functions can be determined using a

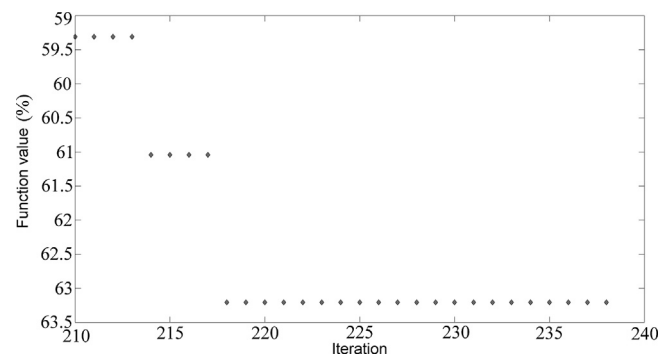


Fig. 1. Results of optimization of un-known constants of Eq. (2) values at each one of iterations of fminsearch optimization algorithm to maximize the percent of good agreement cases.

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