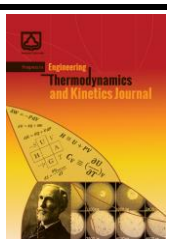
Semnan University

Progress in Engineering Thermodynamics and Kinetics Journal

Journal homepage: https://jpetk.semnan.ac.ir/



Research Article

Application of a simple cubic regularity for liquid density predictions and comparison with GMA EOS

Ali Bakhshi Ani, Seyed Hossein Mazloumi*

Department of chemical engineering, Faculty of engineering, Ferdowsi University of Mashhad, Mashhad, Iran

ARTICLE INFO

Article history:

Received: 202*-**-**

Revised: 202*-**-**

Accepted: 202*-**-**

Keywords:

Regularity;
Liquid density;
Cubic;

ABSTRACT

Based on a cubic regularity, (2Z-1)v is nearly linear versus molar density at isothermal conditions for each liquid, where Z and v are compressibility factor and molar volume, respectively. Using the regularity, a cubic equation of state can be obtained. The temperature-dependent parameters of the cubic EOS are obtained through the correlation of pure liquid density of several substances at various pressures and temperatures. The results of the cubic EOS are in good agreement with the experimental data. In addition, the results of the cubic EOS are compared with the Goharshadi-Morsali-Abbaspour (GMA) EOS.

1. Introduction

Finding the density of liquids in different pressures and temperatures has been one of the considerable issues in thermodynamics from past to present because of its importance in buoyant force, floating objects, etc. So, a lot of experimental studies were done to measure various liquid densities in wide ranges of pressures and temperatures.

* **Corresponding author.**
E-mail address: s.h.mazloumi@um.ac.ir

Cite this article as:

Bakhshi Ani, A., & Mazloumi, H. (2025). Application of a simple cubic regularity for liquid density predictions and comparison with GMA EOS. *Progress in Engineering Thermodynamics and Kinetics*.

https://doi.org/10.22075/jpetk.2023.25732.1005

Simultaneously with the experimental studies, research to find the regularities that relate the density of liquids to pressure and temperature was started. Because of the complex behavior of liquids on the molecular scale, the earlier regularities such as Tait-Murnaghan relation have been applied for years without any theoretical foundation.

In 1993, Parsafar and Mason [2] proposed a model for the density of liquid in which $(Z-1)v^2$ varies linearly with respect to ρ^2 on statistical-mechanical theory but does not predict as great as a range of linearity that is suggested by the experiment. In 2005, Goharshadi et al. [3] introduced regularities for liquids based on average potential energy which is known as GMA EOS. The GMA EOS suggests that $(2Z-1)v^3 = a(T) + b(T)\rho$ where a and b are temperature dependence parameters for each component. The agreements of the results of the GMA equation with experimental data have been shown to be acceptable with minor errors, however, density calculations are rather difficult due to the order of ρ in this equation.

The purpose of this study is to evaluate the accuracy of a simple cubic regularity, suggested by Moosavi and Sabzevari [4], for density calculations of liquids and compare the results with GMA EOS.

2. Theory

To obtain the cubic EOS for calculating the density of liquids, assumptions and principles of LIR and GMA EOS were used. Approximately, the average potential energy is the summation of the effects of nearest neighbors only, therefore [3, 4],

$$U = \frac{N}{2} Z(\rho)\left[\frac{C_n}{r^n} - \frac{C_m}{r^m}\right] \qquad (1)$$

and U can be written as:

$$\frac{U}{N} = \frac{K_n}{V^{\frac{n}{3}+1}} - \frac{K_m}{V^{\frac{m}{3}+1}} \qquad (2)$$

Where K_n and K_m are the corresponding parameters. since:

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \approx \left(\frac{\partial (\frac{U}{N})}{\partial V}\right)_T \qquad (3)$$

By carrying out the derivative, internal pressure may be obtained as,

$$P_i = \left(\frac{m}{3}+1\right) K_m \rho^{\frac{m}{3}+2} - n\left(\frac{n}{3}+1\right) K_n \rho^{\frac{n}{3}+2} \qquad (4)$$

In order to obtain the cubic EOS, it is needed to assume m=0 and n=3. It means that $P_i {v_i}^2$ versus ρ is linear in each isotherm, thus [4],

$$P_i {v_i}^2 = a(T) + b(T)\rho \qquad (5)$$

a and b are temperature dependence parameters. To find the dependence, GMA EOS assumptions for the parameters was used [4],

$$a(T) = A_1 + A_2 T \qquad (6)$$

$$b(T) = B_1 + B_2 T \qquad (7)$$

Using $d\left(\frac{P}{T}\right) = \frac{P_i}{T^2} dT$ and eq. (5) and integration, the regularity can be obtained [4],

$$B(T)\rho^3 + A(T)\rho^2 + \rho - \frac{2P}{RT} = 0 \qquad (8)$$

or,

$$(2Z - 1)\, v = a(T) + b(T)\rho \qquad (9)$$

Where:

Z and v are the compressibility factor and molar volume, and:

$$A(T) = A_0 + \frac{2A_2 lnT}{R} - \frac{2A_1}{RT} \qquad (10)$$

$$B(T) = B_0 + \frac{2B_2 lnT}{R} - \frac{2B_1}{RT} \qquad (11)$$

In which A_0, A_1, A_2, B_0, B_1 and B_2 are constants and they just depend on the component.

3. Result and discussion

To consider the precision of this EOS and compare its result to GMA EOS and experimental data, we did the calculations for 11 components with both EOSs.

First, we plotted isotherms $(2Z - 1)\, v$ versus ρ for 11 liquids in different temperatures and pressures by the cubic EOS using available experimental data [5-10]. Figs. 1 shows these isotherms for 2-Butyne, Krypton, Mercury, Argon, and 2,3-Dimethyl butane.

At the next step, we calculated the densities of these components by cubic EOS and GMA in ranges of temperature and pressure of available experimental data and compared the results acquired.

In Table 1, we summarized the calculations for all studying components and showed the value of R-square and error (=100 $|\rho_{cal} - \rho_{exp}|/ \rho_{exp}$) for both EOSs.

The results of Table 1 clearly show that isotherms $(2Z-1)\,v$ versus ρ are linear and the experimental data confirm this linearity. The cubic EOS could predict the density with an average error of 0.75%, however, the average error of GMA EOS is 0.73%.

By comparing the findings of cubic EOS with GMA EOS, it is obvious that the results of cubic EOS for most of the components are almost near to GMA EOS, even for some cases presents better results, so we can use this cubic EOS as the same as GMA EOS with acceptable errors. The advantage of this equation is that cubic EOSs are more common and can be solved easily as the same as RK or the other cubic equations of state.

The constants of the cubic can be calculated easily in the desired temperature and pressure for different components. Table 2 shows these values for each component that we studied in this work. The procedure of determining the parameters starts with plotting $(2Z-1)v$ versus ρ for various isotherms. The slopes and intercepts of the straight lines can be used to obtain A_0 to A_2 and B_0 to B_2, respectively. This was done by Matlab software.
The fair results for some components may be attributed to the fact that this cubic EOS has no co-volume that affects the results at lower temperatures and higher pressures.

4. Conclusion

From the results, we can find that:

1- Isotherm (2Z-1)v versus ρ is linear and the experimental data support this linearity.
2- The cubic EOS could predict the density of liquids with acceptable errors.
3- The results of the cubic EOS were near to GMA EOS results for most of the components.

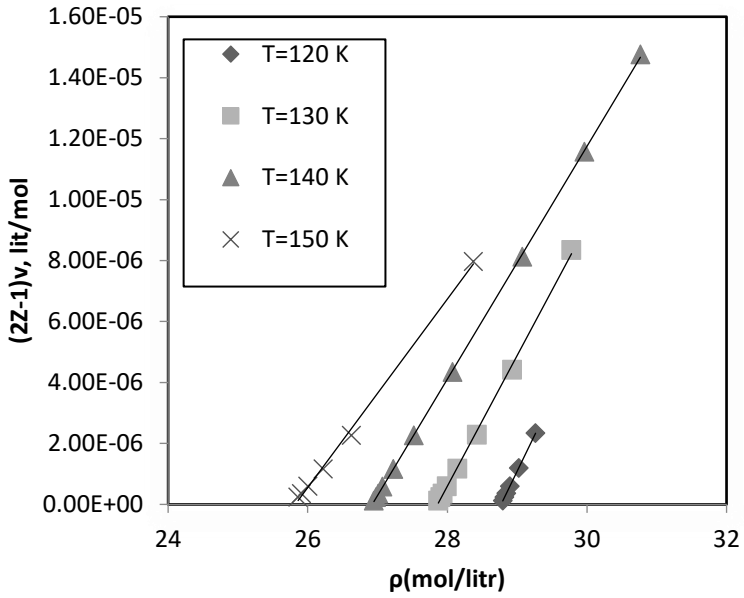


Fig 1. Isotherms $(2Z-1)\,v$ versus ρ for Krypton [5].

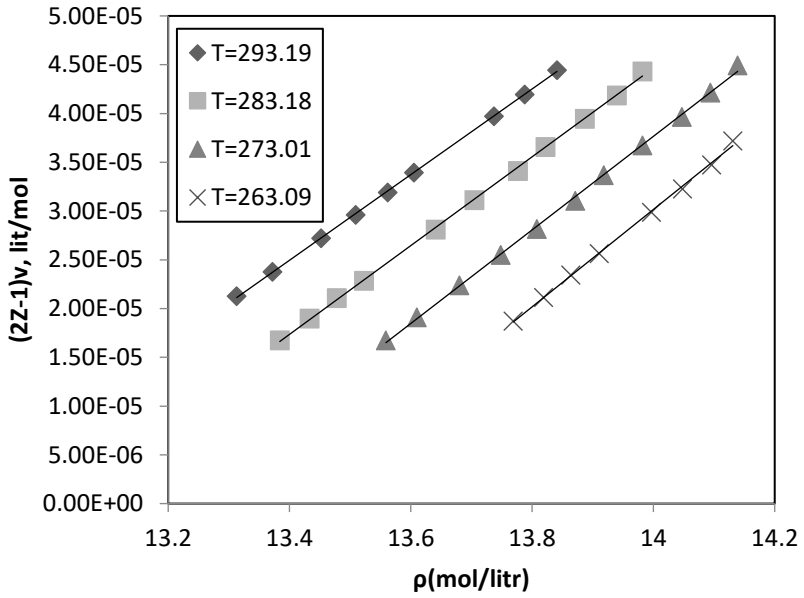


Fig 2. Isotherms $(2Z-1)\,v$ versus ρ for 2-Butyne [6].

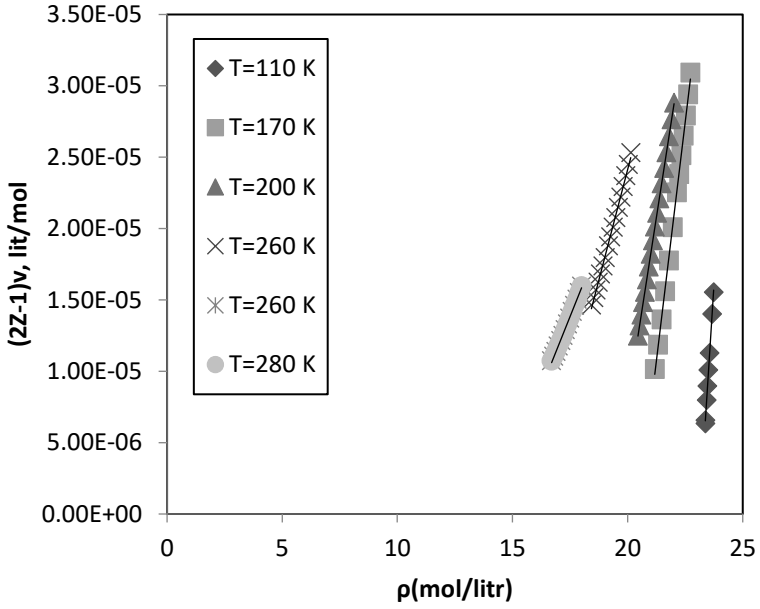


Fig 3. Isotherms $(2Z-1)\,v$ versus ρ for Ethylene [7].

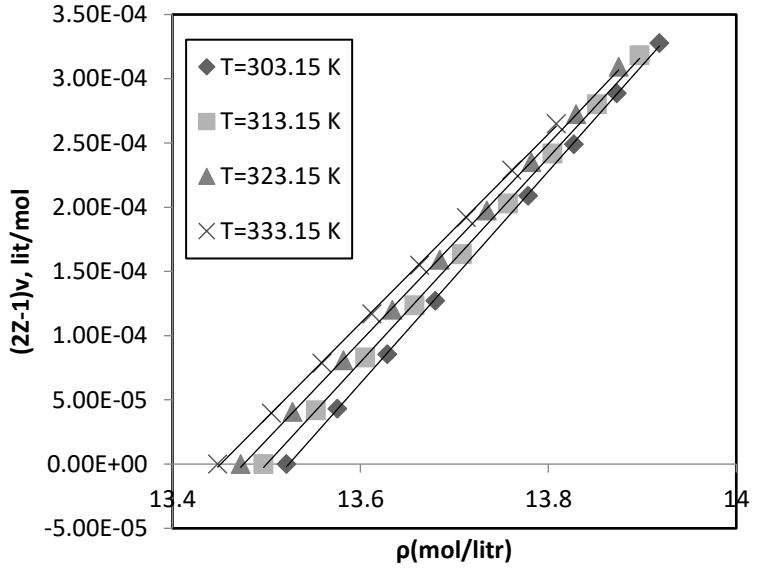


Fig 4. Isotherms $(2Z-1)\,v$ versus ρ for Mercury [8].

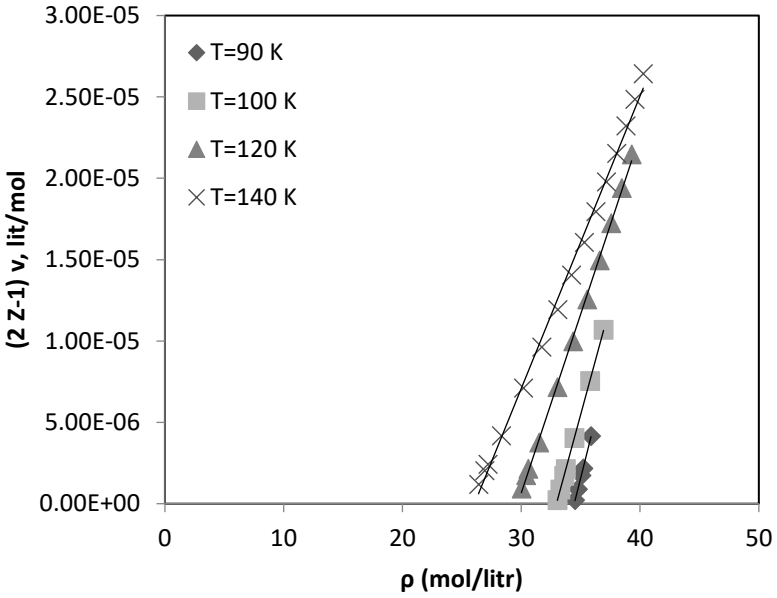


Fig 5. Isotherms $(2Z-1)\,v$ versus ρ for Argon [9].

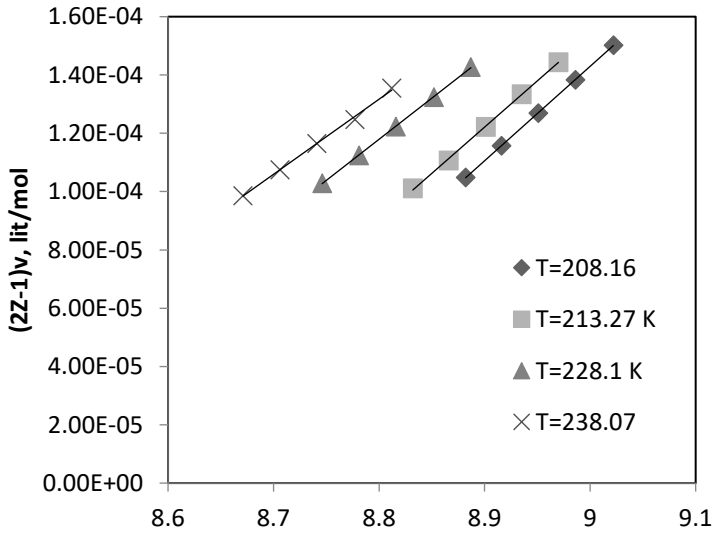


Fig 6. Isotherms $(2Z-1)\,v$ versus ρ for 2,3-Dimethyl butane [10].

Table1. The experimental range of data, the minimum and maximum square of correlation coefficient (R^2) for Cubic EOS and GMA. Experimental data were taken from [5-10].

			Model used in this work		GMA EOS	
Component	T(min)-T(max), K	P(min)-P(max), bar	R^2(min-max)	Error %	R^2(min-max)	Error %
Argon	90-150	10-2400	0.996-0.999	1.294	0.993-1	0.378
2-Butyne	263.09-293.19	349.6-1038.1	0.998-0.999	0.022	0.996-0.999	0.595
Dimethyl butane	208.16-238.07	715.9-1069.1	0.997-0.999	0.068	0.997-1	0.415
Ethylene	110-280	158.46-1150.25	0.997-1	0.483	0.996-1	0.101
krypton	120-150	5-800	0.998-0.999	0.167	0.997-1	0.186
Mercury	303.15-333.15	0-8000	0.999	1.244	1	1.357
Methanol	298.15-353.15	1-1000	0.999	3.491	0.999	2.34
1-ethyl-3-methylimidazoliumethylsulfate	283.14-293.14	40-139.485	0.999-1	0.0131	1	0.005
Tetramethylsilane	198.16-257.91	732.8-1016.9	0.995-0.999	0.0357	0.995-1	0.0384
Water	303.15-333.15	200-1600	0.975-0.994	0.149	0.971-0.994	0.199
Xenon	170-220	5-200	0.998-0.999	1.365	0.999-1	2.451

Table 2. The values of constant parameters for each component for studied systems.

Component	$A_0(\mathrm{L}\,mol^{-1})$	$A_1(L^2 bar\ mol^{-2})$	$A_2(L^2 bar\ K^{-1} mol^{-2})$	$B_0(L^2 mol^{-2})$	$B_1(L^4 bar\ mol^{-3})$	$B_2(L^3 bar\ K^{-1} mol^{-3})$
Argon	-1.52E+01	-6.95E+00	1.14E-01	4.29E-01	2.28E-01	-3.13E-03
2-Butyne	6.26E-01	1.09E+02	1.84E-02	2.02E-01	-6.01E+00	-1.84E-03
Dimethyl butane	-2.37E+04	-3.36E+04	1.54E+02	2.87E+03	4.09E+03	-1.87E+01
Ethylene	-3.49E+00	3.06E+01	3.98E-02	4.71E-01	-8.73E-01	-3.69E-03
krypton	-1.64E+01	-3.84E+00	1.23E-01	9.57E-01	5.69E-01	-6.90E-03
Mercury	-2.97E+03	-5.79E+03	1.83E+01	2.17E+02	4.23E+02	-1.33E+00
Methanol	1.22E+06	-1.37E+07	-1.22E+04	-3.93E+07	3.23E+08	3.63E+05
1-ethyl-3-methylimidazoliumethylsulfate	3.33E+02	4.49E+03	-4.34E-01	-6.66E+02	-1.90E+03	3.87E+00
Tetramethylsilane	-1.01E+03	-1.15E+03	6.60E+00	1.22E+02	1.45E+02	-8.00E-01
Water	2.35E+05	4.24E+05	-1.45E+03	-2.50E+05	-4.48E+05	1.54E+03
Xenon	4.13E+02	5.41E+02	-2.73E+00	-1.96E+01	-2.55E+01	1.30E-01

References

[1] J.R. Macdonald, Rev. Mod. Phys. 41 (1969) 316.

[2] G. Parsafar, E. A. Mason, Linear Isotherms for Dense Fluids: A New Regularity, The Journal of Physical Chemistry, 97 (1993) 9048.

[3] E. K. Goharshadi, A. Morsali, M. Abbaspour, New regularities and an equation of state for liquids, Fluid Phase Equilibria 230 (2005) 170–175.

[4] M. Moosavi, S. Sabzevari, A new equation of state for molten alkali metal alloys, Journal of Molecular Liquids 174 (2012) 117–123.

[5] W. B. Streett and L. A. K. Staveley, Experimental Study of the Equation of State of Liquid Krypton, J. Chem. Phys. 55 (1971) 2495.

[6] V. Garcia Baonza, M. Caceres AIonso, J. Nlez Delgado, Experimental and Theoretical Studles of the Equation of State of Liquid 2-Butyne from248 to 293 K and Pressures up to 104 MPa, The Journal of Physical Chemistry, 96 (1992).

[7] Jorge C. G. Calado,t Paulette Clancy, Andreas Heintz, and WlHlam B. Streett, Experimental and Theoretical Study of the Equation of State of Liquid Ethylene, J. Chem. Eng. Data 27 (1982) 370-305.

[8] T. Grindley and John E. Lind, PVT Properties of Water and Mercury, J. Chem. Phys. 54, (1971) 3983.

[9] W.B. Streett, Thermodynamic properties of liquid argon at high pressures calculated from PVT and sound velocity data, Physica 76 (1974) 59-72.

[10] V. Garcia Baonza,' M. Cdceres Alonso, J. NliAez Delgado, Study of the Equation of State of Liquid 2,3-Dimethylbutane at High Pressures, The Journal of Physical Chemistry, 97 (1993).