

Mathematical Model Simulation of Non-Linear Equations using MATLAB: Specific Volume of Gas with Van der Waals Equation

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Article Info

Article history:

Received: June 15, 2022

Accepted: October 20, 2022

Published: October 30, 2022

Keywords:

MatLab;

Non-Linear Equation;

Specific Volume of Gas;

Van der Waals Equation;

ABSTRACT

Computational physics is concerned with the application of numerical methods in solving physical problems. The van der Waals gas model is one of the most common non-linear models. This study simulated a mathematical model of a non-linear equation using MatLab for the case of the specific volume of gas in the equation of the state of van der Waals. This study aimed to determine the molar volume and compressibility factor, as well as describe the relationship between the compressibility factor and the reduced pressure. The method of the study is experimental. The independent variables are the reduced pressure and temperature values. The dependent variable is the determination of the value of the molar volume (V) and the compressibility factor (Z). The control variable, in the form of a function used in solving this case, is based on the equation $(P + \frac{a}{V^2})(V - b) = RT$ with the gas used is ammonia. The `fzero` command can be used to solve $f(x) = 0$ with a single variable. This program that has been running successfully can show various predictions in the form of reduction pressure, thus obtaining the values of the molar volume and compressibility factor using the ideal gas equation. There is a deviation in ammonia gas, the $Z > 1$ at high reduction pressures, and $Z < 1$ at medium pressures. This study can provide contributions and benefits in the form of material enrichment of thermodynamics to understand how real gases behave. The ideal gas equation can be modified into the van der Waals equation.

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INTRODUCTION

Most technical and scientific problems can be formulated in determining the value of some x variable whose value is zero from some function of that variable. Mathematically, this is represented by equation (1) (Saheya et al., 2016; Shah & Noor, 2015)

$$f(x) = 0. \quad (1)$$

where $f(x)$ is some non-linear algebraic equation.

The procedure for finding a solution (if any) cannot be performed analytically. In some cases, analytical techniques only give tangible results while zero complexities have to be found and reported (Juhari, 2021). Thus, numerical techniques are a viable option to solve these non-linear problems. Not all mathematical models can be easily solved same as using analytical methods, so the solution is using numerical methods.

Numerical methods can help solve problems if mathematically can form a pattern of relationships between

How to cite

Amalia, A. F., Budhi, W., Melati, A. & Nurwijayanto, U. (2022). Mathematical model simulation of non-linear equations using MATLAB: Specific volume of gas with Van der Waals equation. *Jurnal ilmiah pendidikan fisika Al-Biruni*, 11(2), 197-206.

variables/parameters that can be described in the form of functions (Hutagalung, 2017; Muhajir & Djumadila, 2017). The numerical method involves an iterative process and if the iteration process is done manually, it will take a long time and risk human error (Haquey et al., 2018; Ritonga & Suryana, 2019). So, numerical analysis and computers are closely related to solving mathematical problems.

Each of the existing computational procedures has its validity domain with several pros and cons (Cordero et al., 2012; Khdhr et al., 2019; Soleymani, 2013). The results obtained will contain errors and go through a long calculation process that makes it tiring, especially if it is solved manually. Along with the development of computer technology, numerical methods have also improved to solve scientific and engineering problems (Temelcan et al., 2020). They are used to transform physical concepts in the form of mathematical equations through a discretization process that will produce numbers that match the behavior of the system (Sabda et al., 2014).

The concepts of natural phenomena are brought into theory through theoretical physics and experimentation. In addition to these two approaches, it is now accepted that the study of natural phenomena numerically is through computational physics. Computational physics is concerned with the application of numerical methods in solving physical problems. It complements theoretical physics and experimental physics, three common ways to solve problems in physics. Because most physics problems are difficult to solve precisely or may be nonlinear, computational physics involves computer simulation and is often considered a "computer experiment" (Sadiku et al., 2017).

Knowledge of numerical methods is very necessary to be able to know the work function of specific software such as MatLab. In particular cases, Matlab can be used to create software that combines calculation, apparition, and programming. The problems

and solutions are uttered in recognizable mathematical details (Amalia et al., 2020; Sahoo & Pine, 2016). MatLab was originally intended to design control systems, but its rapid development has gained popularity in other fields of science and technology. It has also been widely used in education, particularly in the study of linear algebra and numerical methods (Kurasov, 2020; Sumardi et al., 2022).

The van der Waals gas model is one of the most common non-linear models. The equations of the state of the van der Waals model are stated in the van der Waals gas law in general thermodynamics (Sadhukhan et al., 2021). The postulates of the molecular kinetic theory of gases ignore the volume occupied by gas molecules. All interactions between molecules, both attractive and repulsive, are also ignored in this postulate. But in reality, all gases have a non-zero molecular volume. Furthermore, real gas molecules interact with each other in a way that depends on the molecular structure so that it is different for each gaseous substance. The kinetic energy of the molecules at high temperatures is quite capable of overcoming the intermolecular attractive forces and the effect of a non-zero volume of molecules predominates. The kinetic energy of gas molecules decreases as the temperature is lowered. The point where the molecules are no longer able to overcome the intermolecular attractive forces and the gas melts (condenses into a liquid) is finally reached. Van der Waals modified the ideal gas law to describe the behavior of real gases explicitly by including the effects of molecular size and intermolecular forces (Ball & Key, 2014; Israelachvili, 2011).

Van der Waals proposed improvements to the equation of state for an ideal gas, noting that the gas molecules occupy a larger volume than is assumed in the ideal gas model and exert long-distance forces of attraction between them. Therefore, the gas molecules cannot fill all the volume in a reservoir and the forces on the walls of the reservoir will decrease due to the attraction

between the molecules. Van der Waals considered molecular interaction and molecular size to improve the ideal gas equation (Suzuki & Suzuki, 2015). The research that has been done by Wibowo et al., is to obtain a quantitative value in the form of the van der Waals constant from ambient air samples through an experimental method combined with curve matching. Through the curve matching method, it is obtained that the pressure of the ambient air sample, in addition to being affected by volume, also increases linearly with temperature (Wibowo et al., 2017)

According to this molecular argument, the equation of the state of van der Waals is equation (2) (Berberan et al., 2008; Zhong et al., 2017).

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (2)$$

with $R = 0,0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. As we can see, the van der Waals equation is complex enough that it is not possible to solve it using algebra, so numerical methods are required. The equation of state of van der Waals for gases is also a third-degree polynomial in V that is often written as equation (3) (Prodanov, 2022).

$$pV^3 - (RT + bp)V^2 + aV - ab = 0 \quad (3)$$

A previous study by Utari et al. (2021) developed a physics calculator for thermodynamics using MatLab. The presented calculator is a proof of thermodynamics formula to be applied to questions. The study conducted by Gimenez et al. (2015) presented a way of understanding and computing numerical formulation in thermodynamical problems, the phase transitions of real gases from the point of view of equilibrium thermodynamics.

However, both studies had not described how to simulate a mathematical model of a non-linear equation using MatLab for the case of the specific volume of gas in the equation of the state of van der Waals. This study aimed to determine the molar volume

and compressibility factor, as well as describe the relationship between the compressibility factor and the reduced pressure. The formulation of the problem that arises was how to find the specific volume of gas at a given temperature and pressure to find the right root of the polynomial equation.

METHODS

The method of study was the experimental method. The relationship between the pressure, volume, and temperature of a real gas is expressed by the equation of state. In this study, the van Der Waals equation of state has the form of equation (4).

$$P = \frac{RT}{v - b} - \frac{a\alpha}{v(v + b)} \quad (4)$$

where $P, v,$ and T are pressure, molar volume, and temperature. R is a gas constant, α is a function of temperature, $a,$ and b are empirical constants that are different for each gas.

Parameter data in the MatLab application required in this study consists of three variables as follows;

1. The independent variables are the reduced pressure and temperature values. Values of various reducing pressures are saved in vector form. Iterative calculation by varying the value of the reduced pressure.
2. The dependent variable is the determination of the value of the molar volume (V) and the compressibility factor (Z) at $P = 56 \text{ atm}$ and $T = 450 \text{ K}$ with the following equations (5) and (6).

$$V = \frac{RT}{P} \quad (5)$$

$$Z = \frac{PV}{RT} \quad (6)$$

The compressibility factor is most often determined by equation (6) (Moiseeva & Malyshev, 2019).

3. The control variable, in the form of a function used in solving this case, is

based on equation (2) with the ammonia gas used. We will change the five variables, namely $P, T, V, a,$ and b into three dimensionless variables, namely $\alpha, \beta,$ and Z_C . The variable of α changes according to the attractive term of the equation of state as equation (7).

$$\alpha = \frac{a}{P_C V_C^2} \quad (7)$$

then,

$$a = \alpha P_C V_C^2 \quad (8)$$

Regardless of the equation of state, β is always defined as equation (9) below

$$\beta = \frac{b}{V_C} \quad (9)$$

then,

$$b = \beta V_C \quad (10)$$

As with β , regardless of the equation of state, the definition of Z_C is as follows

$$P_C V_C = Z_C R T_C \quad (11)$$

so that,

$$V_C = \frac{Z_C R T_C}{P_C} \quad (12)$$

Equations (6), (8), and (10) are substituted into the differential equations of equation (2) until finally three equations with unknown variables are obtained as follows

$$1 + \alpha - \frac{1}{Z_C(1-\beta)} = 0 \quad (13)$$

$$\frac{1}{Z_C(1-\beta)^2} - 2\alpha = 0 \quad (14)$$

$$\frac{1}{Z_C(1-\beta)^3} - 3\alpha = 0 \quad (15)$$

By solving equations (13), (14), and (15), it will get the values of $\alpha, \beta,$ and Z_C as follows

$$\alpha = \frac{3}{8} \quad (16)$$

$$\beta = \frac{1}{3} \quad (17)$$

$$Z_C = \frac{3}{8} \quad (18)$$

Equations (16), (17), and (18) are substituted into the definition of

dimensionless variables so that the values of a and b are obtained as equations (19) and (20).

$$a = \frac{27R^2 T_C^2}{64P_C} \quad (19)$$

$$b = \frac{RT_C}{8P_C} \quad (20)$$

with,

T_C = The critical temperature in K (405,5 K for ammonia)

P_C = The critical pressure in atm (111,3 atm for ammonia)

The steps in making the application of the MatLab program in determining the value of the molar volume and the compressibility factor in the van der Waals gas equation in figure 1.

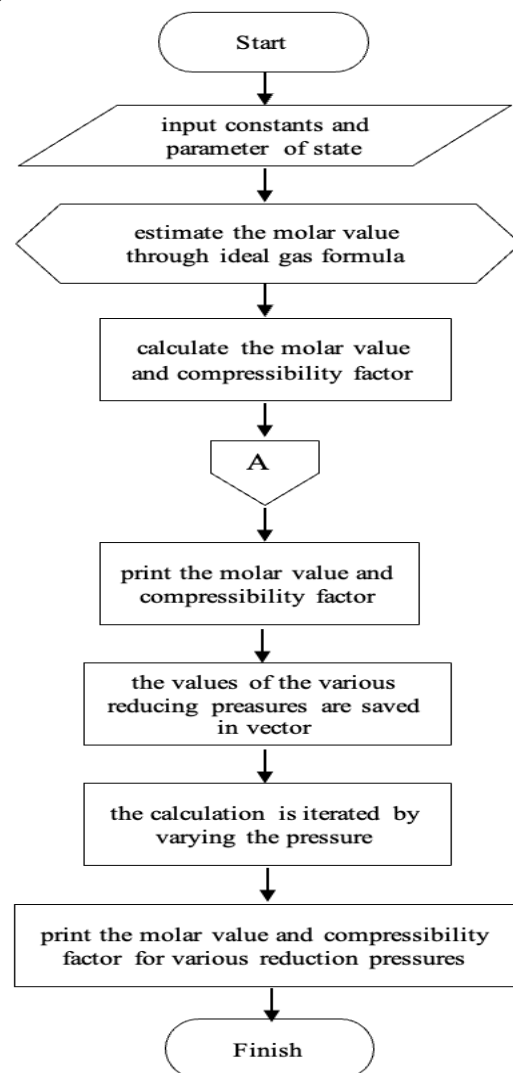


Figure 1. The steps in making the application of the MatLab program

RESULTS AND DISCUSSION

Equation (4) is a polynomial of the third degree in V and can easily be rearranged into the canonical form of the polynomial, as equation (21).

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (21)$$

where $A = \frac{aP}{R^2T^2}$ and $B = \frac{bP}{RT}$. Thus, the problem is to find the specific volume of gas at a given temperature and pressure so that the roots of the polynomial equations become exact.

Equation (4) needs to be rearranged in the form of equation (21) so that it becomes equation (22).

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0 \quad (22)$$

To get the value of V at equation (3), equation (2) become equation (23) as follows

$$f(V) = 0. \quad (23)$$

The value of V containing equation (23) in MatLab can be determined by using the function 'fzero'. The fzero command can be used to solve an equation (1) with a single variable. The user needs to know roughly where the solution is, or if there are multiple solutions, which one is desired (Gilat & Subramaniam, 2014). For regularity and ease of calling, it would be better to define the function in the 'M-file'. MatLab has a variety of functions and operators that allow easy implementation of many numerical methods. In addition, programs can be written as so-called M-files that can be used to implement numerical calculations (Chapra & Canale, 2015).

As the example in this trial, we take ammonia gas at a pressure of $P = 56 \text{ atm}$ and a temperature of $T = 450 \text{ K}$. This program is designed to calculate the molar volume and compressibility factor, using the van der Waals equation of state. Then, the calculation is repeated for various reduction pressure values, namely $P_r = 1, 2, 4, 10$, and

20. The following is the writing of the program for the completion of the research variables.

```
% Main Program : van der Waals
Equation.m
function vanderWaals_fzerofunction
clear all % Clear memory
global P a b R T % Defining the
variables as
% global variable so it can be read
by
% Sub_ProgramVol_Mol.m
% Enter constants and state
parameters
Pc = 111.3; % Critical pressure in
atm
Tc = 405.5; % Critical temperature
in K
R = 0.08206; % Gas constant in
atm.L/mol.K
T = 450; % in K
P = 56; % in atm
% Van Der Waals Constant
a = 27/64*R^2*Tc^2/Pc;
b = R*Tc/(8*Pc);

volguess = R*T/P; % Estimating the
value of the molar volume using the
ideal gas equation
v = fzero(@Vol_Mol, volguess); %
Calculate the molar volume
Z = P*v/(R*T); % Calculate
compressibility factor
disp('Temperature (K) = ');T
disp('and Pressure (atm) = ');P
disp('Obtained the molar vol (L) =
');v
disp('and compressibility factor =
');Z
% The values for various reducing
pressures are stored in vector form
Pred = [1 2 4 10 20];
% Iterative calculation by varying
the pressure
for k = 1: 5
P = Pc*Pred(k);
volguess = R*T/P;
v = fzero (@Vol_Mol,volguess);
Z = P*v/(R*T);
result(k,1) = Pred(k);
result(k,2) = v;
result(k,3) = P*v/(R*T);
end
disp('Obtained the molar vol and Z
factor for the following predictions
:');
disp('-----
-----')
```

```

disp('=====')
disp(' Pred Molar Vol Z factor ')
disp('=====')
disp(result)
disp('=====')

plot(result(:,1),result(:,3),'or-')
title('Graph of the Relationship
between Compressibility Factors and
Reduction Pressure')
xlabel('Reduction pressure, Pr')
ylabel('Compressibility Factor, Z')

function f_V = Vol_Mol(V)
%van der Waals Equation
% [ a ]
% [ P+----- ]( V-b ) = RT
% [V^2]
% Parameters of ammonia63

global P a b R T
% Modification of the van der Waals
equation
f_V = P.*V^3-(P*b+R*T)*V^2+a*V-a*b;

```

This program (Figure 2) that has been running successfully can show various predictions in the form of reduced pressure, thus obtaining the values of the molar volume and compressibility factor using the ideal gas equation.

```

Command Window
New to MATLAB? Watch this Video, see Examples, or read Getting Started.

>> vanderWaalsEquation
Temperature (K) =
T =
    450
and pressure (atm)
P =
    56
Obtained the molar vol (L) =
v =
    0.5749
and compressibility factor =
Z =
    0.8718
f_v obtained the molar vol and Z factor for the following predictions:

Command Window
New to MATLAB? Watch this Video, see Examples, or read Getting Started.

56
Obtained the molar vol (L) =
v =
    0.5749
and compressibility factor =
Z =
    0.8718
obtained the molar vol and Z factor for the following predictions:
-----
Pred    molar vol    Z factor
-----
1.0000    0.2335    0.7038
2.0000    0.0773    0.4658
4.0000    0.0607    0.7313
10.0000   0.0509    1.5334
20.0000   0.0462    2.7835
-----
f_v >>

```

Figure 2. Programming results

The relationship between the compressibility factor and the reduced pressure is shown in Figure 3 which is generated by the program that has been

created. There is a deviation in ammonia gas, the Z value is greater than 1 at high reduction pressures, and less than 1 at medium pressures. Deviations that occur in real gases

can be caused by intermolecular attractive forces and the volume of the molecules cannot be ignored. The occurrence of deviations in the compressibility factor Z is caused by the attractive and repulsive intermolecular forces. Initially, the intermolecular forces of attraction make the gas more compressible than an ideal gas at low pressure. After that, when the pressure increases at a certain temperature and pressure, the repulsive force tends to make its volume larger than that of an ideal gas. When the force of attraction dominates, $Z < 1$. When the repulsive force dominates, $Z > 1$. The relative importance of the attractive forces decreases with increasing temperature (Johnston, 2014).

The compressibility factor is the ideal gas and can be calculated for fluids in critical conditions (Chogle & Maddah, 2015). For ideal gases, the value of $Z = 1$, while for real gases $Z \neq 1$. Thus, the further Z deviates from the value 1, the less ideal the gas is (Kulinskii, 2014; Manikantachari et al., 2017). At very low pressure ($P_r \ll 1$), the gas behave as an ideal gas regardless the temperature.

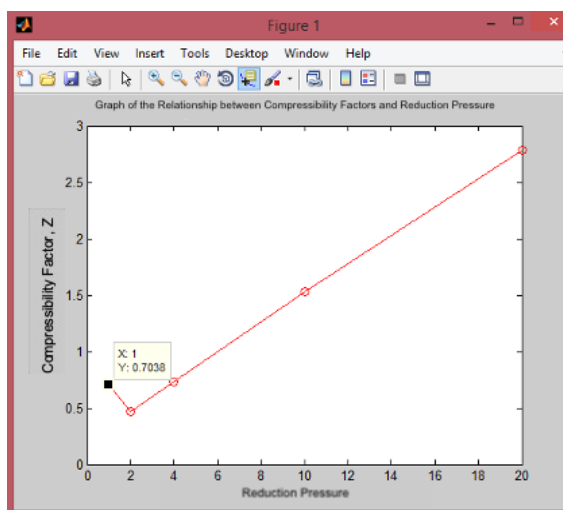


Figure 3. Graph of the relationship between compressibility factor and reduction pressure

This study can provide contributions and benefits in the form of material enrichment in thermodynamics and chemical physics courses.

CONCLUSION AND SUGGESTION

According to the study that has been achieved, the algorithm can be run. The `fzero` command is used for solution estimation. It is important to understand the behaviour of real gases because the ideal gas law does not accurately describe systems under non-ideal conditions such as the compressed state. The results of this study need to be followed up to determine student satisfaction and suitability with the material when using this calculation application. This application also needs to be developed using a GUI (Graphical User Interface). This study can provide contributions and benefits in the form of material enrichment of thermodynamics to understand how real gases behave. The ideal gas equation can be modified into the van der Waals equation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Lembaga Penelitian dan Pengabdian kepada Masyarakat (LP2M UST) for funding the study under an internal grant through SK No. 16/UST/LP3M/PUSLIT/PDU/K/VII/2020.

AUTHORS CONTRIBUTION

AFA constructing and reviewing the literature. WB reviewed the literature and edited the manuscript. AFA, AM, and UN developing programs in Matlab. UN edited the manuscript. All authors read and approve the final manuscript.

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