Ostrowski's fourth-order iterative method speedily solves cubic equations of state

Mehmet Çetin Koçak *

Chemical Engineering Department, Engineering Faculty, Ankara University, 06100 Tandoğan, Ankara, Turkey

ARTICLE INFO

ABSTRACT

Pressure–volume–temperature (P–V–T) data are required in simulating chemical plants because the latter usually involve production, separation, transportation, and storage of fluids. In the absence of actual experimental data, the pertinent mathematical model must rely on phase behaviour prediction by the so-called equations of state (EOS). When the plant model is a combination of differential and algebraic equations, simulation generally relies on numerical integration which proceeds in a piecewise fashion unless an approximate solution is needed at a single point. Needless to say, the constituent algebraic equations must be efficiently re-solved before each update of derivatives. Now, Ostrowski's fourth-order iterative technique is a partial substitution variant of Newton's popular second-order method. Although simple and powerful, this two-point variant has been utilised very little since its publication over forty years ago. After a brief introduction to cubic equations of state and their solution, this paper solves five of them. The results clearly demonstrate the superiority of Ostrowski's method over Newton's, Halley's, and Chebyshev's solvers.

1. Introduction

Successful design and operation of chemical plant require in depth knowledge of the pertinent processes. Simulation with a mathematical model can contribute to understanding how the plant behaves under widely different conditions. Large dimensionality, non-linearity, and interaction among process variables notoriously characterise chemical plant models and frequently necessitate computer usage in this activity. Numerical solution techniques are harnessed very often because an analytical answer is either unavailable or intractable. Numerical integration proceeds in a piecewise fashion unless an approximate solution is needed at a single point. Obviously, the constituent algebraic equations must be efficiently re-solved before each update of derivatives.

The objective of this work is to re-introduce Ostrowski's fourth-order solver as a two-point partial substitution variant of Newton's method and investigate the relative boost it can render in iterative solution of cubic EOS and therefore in chemical plant simulation.

2. Materials and method

2.1. Cubic equations of state (EOS)

This subsection is largely based on a comprehensive *courseware module* created in [1]. As the name implies, an EOS defines the state of a fluid and can be used as the basis for generating data such as densities (vapour and liquid), vapour pressures

---

* Tel.: +90 312 203 34 38.
  E-mail address: kocak@eng.ankara.edu.tr.

of pure components, critical pressures and temperatures for the mixture, vapour–liquid equilibrium (VLE) information, and thermodynamic properties.

Since the time of the ideal gas law (ideal gas EOS), a great number of EOS have been proposed to describe real gas behaviour but only relatively simple a few have persisted through the years. Generally, the more complex the EOS, the more accurate it is. However, this is not always the case; sometimes a rather simple EOS can do a very good job. There have been a number of attempts to derive a theoretically sound EOS but, generally speaking, not much success has been achieved along that line. As a result, most EOS used today are semi-empirical in nature, this being so because their parameters are *fitted* to available data.

EOS are generally devised for *pure* substances. Their application to *mixtures* requires knowledge of composition and an appropriate mixing rule. EOS development assumes that the system is at equilibrium. Admittedly, this is not a perfect assumption but is a reasonable one. At equilibrium, the three variables needed to completely define the state are pressure, volume, and temperature. In other words, the functional form of an EOS can be expressed as $f(P, V, T) = 0$.

P–V isotherms for a pure substance at sub-critical conditions ($T < T_c$) have a discontinuity at the vapour–liquid transition; as pressure increases, there arises a point of discontinuity that represents the phase change. This is a challenge for all EOS. What is required here is fitting a *continuous* mathematical *function* to a *discontinuous*, real-life *event*. Strictly, this requirement is contradictory. Even though neither cubic nor any other continuous mathematical function is able to follow the discontinuity in real P–V isotherms, what they can do is good enough for engineering purposes. The *cubic* behaviour can reasonably match the liquid and vapour branches for the real, experimental isotherms.

Let v, T, and R be molar volume, absolute temperature, and the universal gas constant, respectively. The following equation will be immediately recognised as *the ideal gas EOS*:

$$Pv = RT. \tag{1}$$

It is obvious that *ideal gas will not condense, no matter what pressure it is subjected to, regardless of the temperature of the system*. In other words, since the ideal gas EOS is continuous it cannot *reproduce* the P–V behaviour of a pure substance. Nevertheless, it can *approximate* real P–V isotherms at low pressures (close to atmospheric) and high temperatures.

An ideal gas is an imaginary gas that satisfies the following conditions: (a) Negligible interactions between the molecules, (b) its molecules occupy no volume, (c) collisions between molecules are perfectly elastic—that is, no energy is lost after collision.

In reality, no gas behaves ideally. Therefore, the ideal gas EOS is not useful for practical applications. It is important however as the basis of understanding of gas behaviour and as the starting point of all modern approaches.

A monumental breakthrough by van der Waals in 1873 won for him a Nobel Prize. In his Ph.D. Thesis, he proposed to semi-empirically remove the key *weaknesses* that the ideal EOS carried with it. The proposal accounted for the non-zero molecular volume and non-zero force of attraction of a real substance by correcting the pressure and volume in the ideal model. The *modified ideal EOS* (or *vdW EOS*) is

$$(P + a/v^2)(v - b) = RT. \tag{2}$$

Imposition of the so-called criticality conditions on (2) leads to expressions for the parameters a and b as functions of critical properties: $a = 27R^2T_c^2/(64P_c)$ and $b = RT_c/(8P_c)$.

To extend this concept to a system of more than one component, one needs a *mixing rule*. He suggested a linear mixing rule and a quadratic mixing rule to weight the contributions of each component using their mole compositions.

The principle of corresponding states (PCS) was stated by van der Waals and reads "*Substances behave alike at the same reduced states. Substances at the same reduced states are at corresponding states*". Reduced properties provide a measure of the departure of the conditions of the substance from its own critical conditions and are defined as follows:

$$P_r = P/P_c, \qquad T_r = T/T_c, \qquad v_r = v/v_c, \qquad v_c = 3RT_c/(8P_c).$$

The *reduced* form of the vdW EOS is obtained by inserting these reduced quantities into (2) and simplifying:

$$(P_r + 3/v_r^2)(3v_r - 1) = 8T_r. \tag{3}$$

This *universal* equation is basically used for thermodynamic correlations. Most thermodynamic correlations have been made viable and general because of the application of the principle of corresponding states.

The vdW EOS (2) can be rearranged into

$$v^3 - (b + RT/P)v^2 + (a/P)v - ab/P = 0, \tag{4}$$

$$Z^3 - \left(1 + \frac{bP}{RT}\right)Z^2 + \left(\frac{aP}{R^2T^2}\right)Z - \frac{abP^2}{(RT)^3} = 0. \tag{5}$$

As observed, the first of these equations is cubic in molar volume v and the second is cubic in compressibility factor Z. By definition, $Z = Pv/(RT)$. So, the vdW EOS is a *cubic* EOS as are all the transformations and modifications that it has undergone since its publication in 1873.

In summary, the contribution of the vdW EOS was manifold: (a) It was the first to predict the continuity of matter between gas and liquid, (b) it radically improved the predictive capability over ideal gas EOS, (c) it formulated the PCS, and (d) it laid foundations for modern cubic EOS.

The achievements of van der Waals are still recognised as crucial in revolutionizing the thinking about EOS. The vdW EOS is talked about because of pedagogical reasons, not because it finds any practical application in today's world. In fact, the vdW EOS is *not* used for any practical design purposes. However, most of the EOS being used widely today for practical design purposes have been derived from the vdW EOS.

The most popular and reliable cubic EOS are: (a) Redlich–Kwong EOS, (b) Soave–Redlich–Kwong EOS (very popular among chemical engineers), and (c) Peng–Robinson EOS (very popular among petroleum and natural gas engineers). There are other more complex EOS: Lee–Kesler EOS, Benedict–Webb–Rubin EOS, and Benedict–Webb–Rubin–Starling EOS.

Cubic EOS are explicit in P but the latter is not the common unknown to be calculated in the typical problem. More probably, P and T are known and v (or its reciprocal, molar density) or Z (the most likely case) is needed. Hence, the application requires a numerical or analytical technique to solve a cubic function. This will be considered in the next subsection.

Cubic equations are S-shaped and have three roots. Either one or all three of them will be real. Since cubic EOS deal with physical quantities (v or Z), only real roots are of interest to engineers. More specifically, v must be greater than b and Z must be greater than $Pb/(RT)$. The possibility of three real roots is restricted to the case of sub-critical conditions ($T < T_c$). If there are indeed three v roots here, then the smallest is assigned to liquid and the largest to vapour; the intermediate root is discarded as it is physically meaningless. Anywhere else only one real root is expected. The largest root is always the correct choice for the gas phase molar volume of pure components.

2.2. Analytical solution of cubic equations

Adewumi [1] describes an analytical way to find the real roots of the cubic polynomial $f(x) = x^3 + c_2x^2 + c_1x + c_0$. The procedure can be summarised as follows. Let

$$Q_1 = (c_2^2 - 3c_1)/9, \qquad Q_2 = (2c_2^3 - 9c_1c_2 + 27c_0)/54, \qquad M = Q_2^2 - Q_1^3, \qquad \theta = \cos^{-1}(Q_2/Q_1^{3/2}).$$

If $M < 0$, there are three distinct roots. Calculate them as:

$$x_1 = -2\sqrt{Q_1}\cos\left(\frac{\theta}{3}\right) - \frac{c_2}{3}, \qquad x_2 = -2\sqrt{Q_1}\cos\left(\frac{\theta + 2\pi}{3}\right) - \frac{c_2}{3}, \qquad x_3 = -2\sqrt{Q_1}\cos\left(\frac{\theta - 2\pi}{3}\right) - \frac{c_2}{3}.$$

If $M > 0$, then there is only one real root given by $x_1 = \sqrt[3]{-Q_2 + \sqrt{M}} + \sqrt[3]{-Q_2 - \sqrt{M}} - c_2/3$.

2.3. Numerical solution of cubic equations

Note the complexity and overhead of this analytical process. There are many numerical alternatives to chose from. These generally involve the solution of $x = g(x)$ by a repetitive scheme $x_{k+1} = g_k = g(x_k)$ where k is the iteration count. The *fixed-point z* of the iteration function g is a *zero* (root) of f. Let $\varepsilon_k = x_k - z$. Suppose there exist a real number n and a non-zero constant c such that $\lim_{k \to +\infty}(|\varepsilon_{k+1}|/|\varepsilon_k|^n) = c$. Then n and c are respectively called the *convergence order* and the *asymptotic error constant*. According to Traub [2], if n is integral, then $c = \lim_{k \to +\infty} \varepsilon_{k+1}/\varepsilon_k^n = g^{(n)}(z)/n!$.

Linear or *first-order* methods ($n = 1$) are those where $g'(z) \neq 0$ and ε_{k+1} is proportional to ε_k in the neighbourhood of z. *Quadratic convergence* ($n = 2$) means that $g'(z) = 0$, $g''(z) \neq 0$, and ε_{k+1} is proportional to ε_k^2 near z. *Cubic* or *higher convergence* ($n > 2$) occurs if $g'(z) = g''(z) = \cdots = g^{(n-1)}(z) = 0$ and $g^{(n)}(z) \neq 0$.

Note that when functions are written in this text without an argument the latter is x. Let g be defined and differentiable on an interval I with all values $g(x) \in I$. Further, let K be a constant. If $|g'| \leq K < 1$ on I, then, as proved in [3], g has a unique fixed-point z on I and the sequence $\{x_k\}$ converges to z for any choice of $x_1 \in I$. Moreover, $\lim_{x \to \infty}(\varepsilon_{k+1}/\varepsilon_k) = g'(z)$. If, in addition, $0 \leq g' \leq K < 1$, then convergence is monotonic, that is, without oscillation. In practice, however, it is difficult to determine a priori the bounds of the convergence interval I.

Newton's popular technique [2–8], is a computationally simple method given by

$$g_N = x - f/f'. \tag{6}$$

It is a piecewise linearization of f since it extends the current tangent to intersect the x-axis and suggests this value as the next approximation to z. As shown by Traub [2], $n_N = 2$ and $c_N = f''(z)/(2f'(z))$ for simple roots. By direct differentiation,

$$g_N' = ff''/f'^2 = L \tag{7}$$

where L is called the logarithmic degree of convexity. Thus, the convergence condition of g_N is that $|L| \leq K < 1$ in the vicinity of z.

Repetition of z means $f'(z) = 0$ also. This demotes g_N's convergence from quadratic to *superlinear* or *geometrical* and slows down the iteration process. If r is the multiplicity of z, then $g'(z) = (r - 1)/r \neq 0$ and $g_{Nr} = x - rf/f'$ restores second-order convergence [6]. Two possibilities are worthy of mention where g_N may fail. First, it can oscillate around a local minimum or maximum of f in the neighbourhood of a simple root. Secondly, it can diverge to another root when f' is small making the value of f/f' too large.

Table 1
Test cases II–V come from [1].

Case	Function	Roots
II	$v^3 - 7.8693v^2 + 13.3771v - 6.5354$	5.7357
III	$v^3 - 15.6368v^2 + 30.315v - 14.8114$	0.807582, 1.36174, 13.4675
IV	$z^3 - 1.0595z^2 + 0.2215z - 0.01317$	0.8045
V	$z^3 - z^2 + 0.089z - 0.0013$	0.0183012, 0.0786609, 0.903038

Applied to Newton's scheme, partial substitution gives $g_{Nps} = x - Gf/f'$ where G is a *gain*. Note that g_{Nr} is a g_{Nps} with a fixed gain $G = r$. There are many well known, third-order g_{Nps} like Halley's and Chebyshev's solvers [8]:

$$g_H = x - Gf/f', \quad G = (1 - L/2)^{-1} = 1 + L/2 + L^2/4 + \cdots, \tag{8}$$

$$g_C = x - Gf/f', \quad G = 1 + L/2. \tag{9}$$

Notice that L requires both f' and f''.

Ostrowski's fourth-order solver is also a g_{Nps}. Its definition is [2]:

$$g_O = x - Gf/f', \quad G = 1 + f(g_N)/(f - 2f(g_N)) = (f - f(g_N))/(f - 2f(g_N)). \tag{10}$$

As is clear, this powerful, two-point method is an attempt to improve Newton's technique by utilising two f values and one f' value at each iteration. Unlike g_C and g_H, there is no need for f''. The next section presents applications to solve cubic EOS numerically and shows that Ostrowski's little-known method really deserves more attention than it has received so far. If g_N is convergent, then g_O should be expected to accelerate the solution.

Irrespective of its convergence order n, there is always a risk that an iterative method may diverge if trials are not started close enough to z. According to Adewumi [1], if the aim is to solve Eq. (5), the usual recommendation is to begin with $z_1 = bP/(RT)$ for the liquid phase and $z_1 = 1$ for the vapour root. Of course, an *educated* guess for the largest root of (4) would be the *ideal* answer $v_1 = v_{id} = RT/P$.

Suppose $f(v) = v^3 + c_2 v^2 + c_1 v + c_0$ is the function to be solved. Comparison with (4) renders the results $b = -c_0/c_1$, $c_2 = -b - RT/P = -b - v_{id}$, and so $v_1 = v_{id} = -c_2 + c_0/c_1$. What if $f(Z) = Z^3 + c_2 Z^2 + c_1 Z + c_0$ is the function to be solved? Comparison with (5) shows that iterations for the liquid phase root should start from $z_1 = bP/(RT) = -1 - c_2$.

2.4. Description of test cases

Taken from [3], Case I is a search for the molar volume of carbon dioxide at $P = 10$ atm (or 1013.250 KPa) and $T = 300$ K. Harnessing $a = 188.33$ Pa m^6 kg^{-2} = 36,461 Pa m^6 kmol^{-2}, $b = 9.77 \times 10^{-4}$ m^3 kg^{-1} = 0.0430 m^3 kmol^{-1}, and $R = 8.314$ kJ kmol^{-1} K^{-1} in (4) yields the equation $f(v) = v^3 - 2.5046v^2 + 0.3598v - 0.0155 = 0$. The ideal gas law gives the educated guess as $v_1 = v_{id} = RT/P = 2.46158401$ m^3 kmol^{-1}. Note that f has a local maximum at $v = 0.0752$ m^3 kmol^{-1} and a local minimum at $v = 1.5945$ m^3 kmol^{-1}. Convergence problems can occur if the starting point is less than the latter.

The remaining four test cases in Table 1 are from Adewumi [1]. Only the largest root (say E) is located in the current work using numerical solvers g_N or g_O. Once E is found, the other two roots can be deduced by a reduction technique. Adewumi [1] sets $F_1 = c_2 + E$ and $F_2 = -c_1/E$ and obtains the remaining roots as $(-F_1 + \sqrt{F_1^2 - 4F_2})/2$ and $(-F_1 - \sqrt{F_1^2 - 4F_2})/2$.

3. Results and discussion

A flexible Matlab program was written to implement the desired solvers. Iteration was stopped when absolute f or absolute change in v (or Z) was less than 10^{-8}. Table 2 depicts the progress of g_N, g_C, g_H, and g_O in Case I. It is evident that g_N requires 4 iterations for convergence while the others need only 3. As expected, f vanishes fastest with g_O. Table 3 depicts the progress of g_N and g_O in Cases II–V. Superiority of Ostrowski's method is clear again.

Newton's method is the usual choice when equations of state are to be solved. This work has shown that a switch to Ostrowski's iterator can be highly beneficial especially in dynamic simulation where these equations are re-solved at each step prior to derivative updates. It must be remembered, however, that this two-point method is a partial substitution variant of Newton's famous second-order solver.

4. Conclusions

Analytical and numerical solution techniques for cubic equations of state (EOS) are the subject of this article. These were treated after a brief description of their role in chemical plant simulation and a review of their historical development. Ostrowski's little-known fourth-order iterator is a two-point method that is a partial substitution variant of Newton's famous second-order solver. As in many other applications, Ostrowski's method has shown superiority here over Newton's technique.

Table 2
Test results using g_N, g_C, g_H, and g_O.

Case	Method	v	f	f'	g_N	g_C	g_H	g_O
I	Newton	2.46158401	0.60982389	6.20759771	2.36334570	2.35575864	2.35512363	2.35458547
		2.36334570	0.04614940	5.27770876	2.35460149	2.35453506	2.35453455	2.35453417
		2.35460149	0.00034994	5.19774560	2.35453417	2.35453416	2.35453416	2.35453416
		2.35453417	0.00000002	5.19713170	2.35453416	2.35453416	2.35453416	2.35453416
	Chebyshev	2.46158401	0.60982389	6.20759771	2.36334570	2.35575864	2.35512363	2.35458547
		2.35575864	0.00637058	5.20830097	2.35453548	2.35453417	2.35453417	2.35453416
		2.35453417	0.00000001	5.19713169	2.35453416	2.35453416	2.35453416	2.35453416
	Halley	2.46158401	0.60982389	6.20759771	2.36334570	2.35575864	2.35512363	2.35458547
		2.35512363	0.00306514	5.20250754	2.35453447	2.35453416	2.35453416	2.35453416
		2.35453416	0.00000000	5.19713167	2.35453416	2.35453416	2.35453416	2.35453416
	Ostrowski	2.46158401	0.60982389	6.20759771	2.36334570	2.35575864	2.35512363	2.35458547
		2.35458547	0.00026668	5.19759953	2.35453417	2.35453416	2.35453416	2.35453416
		2.35453416	0.00000000	5.19713167	2.35453416	2.35453416	2.35453416	2.35453416

Table 3
Iteration outputs for the last four test cases.

Case	Method	v or z	f	g_N	g_O
II	Newton	7.380749	65.583559	6.299240	5.818682
		6.299240	15.429513	5.835573	5.738841
		5.835573	2.271284	5.739718	5.735709
		5.739718	0.087669	5.735711	5.735704
		5.735711	0.000150	5.735704	5.735704
	Ostrowski	7.380749	65.583559	6.299240	5.818682
		5.818682	1.873791	5.738504	5.735706
		5.735706	0.000055	5.735704	5.735704
III	Newton	15.148217	332.292349	13.791817	13.479861
		13.791817	52.345552	13.483245	13.467516
		13.483245	2.421372	13.467526	13.467486
		13.467526	0.006127	13.467486	13.467486
		13.467486	0.000000	13.467486	13.467486
	Ostrowski	15.148217	332.292349	13.791817	13.479861
		13.479861	1.900490	13.467510	13.467486
		13.467486	0.000000	13.467486	13.467486
IV	Newton	1.000000	0.148830	0.865007	0.811511
		0.865007	0.032902	0.813050	0.804691
		0.813050	0.004005	0.804738	0.804532
		0.804738	0.000095	0.804532	0.804531
		0.804532	0.000000	0.804531	0.804531
	Ostrowski	1.000000	0.148830	0.865007	0.811511
		0.811511	0.003266	0.804671	0.804531
		0.804531	0.000000	0.804531	0.804531
V	Newton	1.000000	0.087700	0.919467	0.903504
		0.919467	0.012449	0.903636	0.903039
		0.903636	0.000437	0.903039	0.903038
		0.903039	0.000001	0.903038	0.903038
	Ostrowski	1.000000	0.087700	0.919467	0.903504
		0.903504	0.000340	0.903038	0.903038

References

[1] M. Adewumi, PNG 520 phase relations in reservoir engineering, Pennsylvania State University, retrieved September 9, 2009 from https://www.e-education.psu.edu/png520/resources/l1.html.
[2] J.F. Traub, Iterative Methods for Solution of Equations, Prentice-Hall, Englewood Cliffs, NJ, 1964.
[3] A.F. Quarteroni, R. Sacco, F. Saleri, Numerical Mathematics, Springer-Verlag, New York, 2000.
[4] K.E. Atkinson, An Introduction to Numerical Analysis, John Wiley and Sons, New York, 1978.
[5] L.V. Fausette, Numerical Methods: Algorithms and Applications, Prentice-Hall, New Jersey, 2003.
[6] C.-E. Fröberg, Introduction to Numerical Analysis, second ed., Addison-Wesley Publishing Co., Reading, 1972.
[7] R.G.E. Franks, Modeling and Simulation in Chemical Engineering, John Wiley Interscience, New York, 1972.
[8] M.Ç. Koçak, Simple geometry facilitates iterative solution of a nonlinear equation via a special transformation to accelerate convergence to third order, J. Comput. Appl. Math. 218 (2) (2008) 350–363.