Calculation of Densities from Cubic Equations of State

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Some cubic equations of state can eventually have unphysical solutions for the molar volume. The conditions for this phenomenon are discussed. The computational accuracy and computing time requirements of the analytical root finding method (Cardano's formula) are investigated. A new, faster iterative root finder for cubic polynomials is proposed.

Introduction

In spite of their theoretical shortcomings, cubic equations of state are still frequently used in many chemical and engineering applications. This is partly due to the fact that these equations can be transformed into cubic polynomials with respect to the molar volume.

This reducibility to a cubic polynomial is by no means required by physical insight, but by mathematical convenience: the calculation of the density or the molar volume from the given pressure and temperature, which is one of the most frequently performed operations in phase equilibrium calculations, can be done for these equations by Cardano's formula. Its application does not require iteration or predetermined initial values, and if more than one solution is possible, it yields all of them. It is easy to program, fail-safe, and fast.

Usually the solution with the highest density (if there is more than one) is associated with the liquid phase, the one with the lowest density with the vapor phase, and thus the road to the calculation of phase equilibria seems clear. It will be shown, however, that there are pitfalls along this road, and that some cubic equations of state can generate unphysical solutions.

The admittedly fast execution of the density calculation is evidently an advantage over noncubic equations, which require higher-order or iterative root solvers. These require typically 2–4 times as much CPU time as Cardano's formula, and it has been argued that this would slow down complex design programs in chemical engineering to a rather unacceptable degree.

One might ask how these design programs could perform satisfactorily a few years ago, when the computers were significantly slower than nowadays, but that is not the objective of this work. Nevertheless, if the computational speed of the density calculation is essential, it might be worthwhile to look for alternatives to Cardano's formula.

Cardano's Formula and Cubic Equations of State

Typical cubic equations of state are of the form

$$p = p^{\mathrm{rep}} + p^{\mathrm{att}} \tag{1}$$

where the repulsion term p^{rep} and the attraction term p^{att} are simple rational functions of the molar volume; for the former usually (but not necessarily) the van der Waals term is used

$$p^{\mathrm{rep}} = \frac{RT}{V_m - b} \tag{2}$$

It should be noted that modern statistical thermodynamics does not support this repulsion term. There is, however, a cubic equation of state for an attractive-hard-sphere fluid, which does not use the van der Waals term (Yelash et al., 1999), but it is not considered here.

By multiplying a cubic equation of state by the denominator polynomials, it is turned into a cubic polynomial equation

$$\sum_{i=0}^{3} s_i V_{\mathrm{m}}^i = 0 \tag{3}$$

from which the molar volume can be readily determined by Cardano's formula, which is outlined below:

Algorithm 1: Cardano's method for solving cubic equations

Given is a polynomial equation with real coefficients a_i

$$a_3 x^3 + a_2 x^2 + a_1 x + a_0 = 0 \qquad \text{with} \qquad a_3 \neq 0$$

1. Divide by a_3 to obtain the normalized form

$$x^3 + b_2 x^2 + b_1 x + b_0 = 0 \qquad \text{with} \qquad b_i = \frac{a_i}{a_3}$$

2. Substitute $x = y - b_2/3$ to eliminate the quadratic term

$$y^3 = px + q = 0 \qquad \text{with} \quad p = b_1 - \frac{b_2^2}{3}$$

$$q = b_0 - \frac{b_1 b_2}{3} + \frac{2 b_2^3}{27}$$

3. Evaluate the discriminant

$$d = \left(\frac{p}{3}\right)^3 + \left(\frac{q}{2}\right)^2$$

4. If $d > 0$, there is only one real root

$$x_0 = \sqrt[3]{-\frac{q}{2} + \sqrt{d}} + \sqrt[3]{-\frac{q}{2} - \sqrt{d}} - \frac{b_2}{3}$$

Otherwise, there are three real solutions

$$x_k = 2\sqrt{-\frac{p}{3}}\,\cos\left(\frac{\phi + 2\pi k}{3}\right) - \frac{b_2}{3}, \qquad k = 0, \ldots, 1,2,3$$

$$\text{with} \qquad \phi = \arccos\left(-\frac{q}{2}\sqrt{-\frac{27}{p^3}}\right)$$

The evaluation of Cardano's formula involves several referrals to root or trigonometric functions. This can lead to a significant loss of numerical precision, even if double-precision numbers are used throughout the computer program.

We checked the accuracy of the molar volumes obtained by Cardano's formula against results obtained by iterative methods. The theoretical precision of a double-precision number is approximately 10^{-15}. The relative error of the volume calculation is very close to this limit for gas volumes; on the liquid side, however, the relative errors can be as high as 10^{-8}. For many thermodynamic calculations, this is not acceptable.

A different pattern of numerical errors is obtained if the cubic polynomial is constructed in terms of densities instead of molar volumes. The relative errors on the gas branch are now insignificantly higher (up to 10^{-13}), but the large deviations on the liquid side are completely avoided. Thus, using densities or concentrations seems to be preferable to using molar volumes.

Another simple way of reducing the computational errors of the volume calculation is to follow the evaluation of Car-
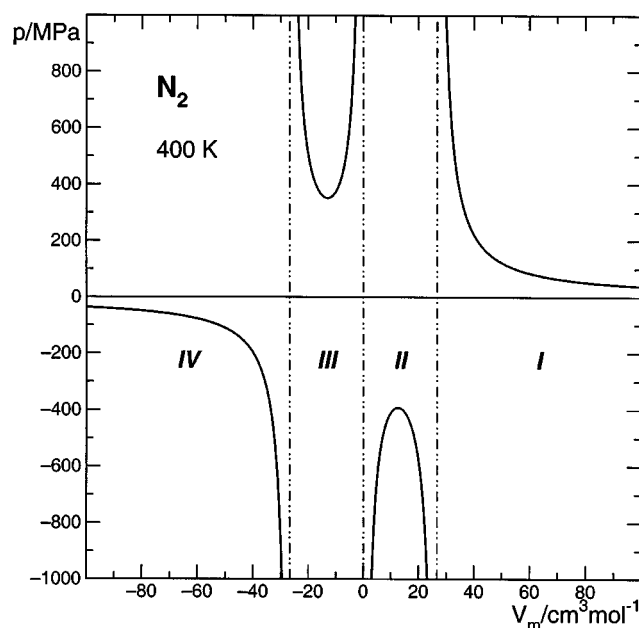

Figure 1. 400 K isotherm of nitrogen, including physically unreasonable branches, calculated with the Redlich–Kwong equation of state.

dano's formula with a Newton iteration

$$V_m' = V_m - \frac{\displaystyle\sum_{i=0}^{3} s_i V_m^i}{\displaystyle\sum_{i=1}^{3} i s_i V_m^i} \tag{10}$$

Here V_m denotes the "raw" result from Cardano's formula. Usually a single iteration step is sufficient.

Unphysical Roots

In view of the well-established user-friendly behavior of cubic equations of state, it may seem surprising that many of them are able to generate unphysical—even negative—molar volumes at supercritical pressures or temperatures. An example can be seen in Figure 1, which shows an isotherm of the Redlich–Kwong equation of state (Redlich and Kwong, 1949) for a wide range of volumes, including "unphysical" values. Evidently, even this widely used equation describes states with positive pressure, but with molar volumes less than its covolume parameter, b. The common practice of identifying the lowest root of Cardano's formula with the liquid volume could eventually lead to undesirable results; for example, at 400 MPa, Cardano's formula would return a negative molar volume!

This insight is not really new. A discussion of the unphysical roots as well as several diagrams similar to Figure 1 can be found in the work of Stamoulis (1994) and even in some older publications (Savini et al., 1965; Mohamed and Holder, 1987).
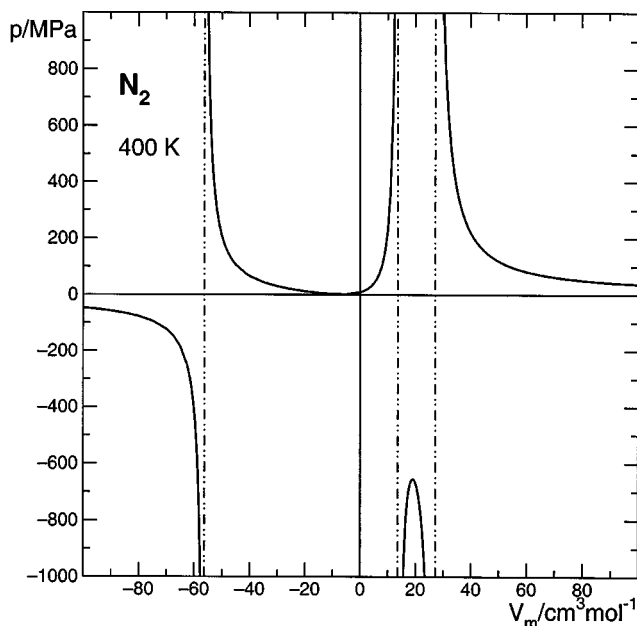
Figure 2. 400 K isotherm of nitrogen, including physically unreasonable branches, calculated with the Trebble–Bishnoi–Salim equation of state.

In the case of the Redlich–Kwong equation of state the appearance of negative roots is limited to rather high pressures, far beyond the typical range of applicability of this equation, so these negative roots are of no practical importance. But there are other equations of state where the unwanted roots can occur at lower pressures, for example, the Trebble–Bishnoi–Salim (TBS) equation (Salim and Trebble, 1991). Figure 2 shows that here negative molar volumes are calculated for *all* positive pressures.

It should be noted that the possibility of having negative roots must not be regarded as a weakness of the TBS equation: the equation works well where it is supposed to work. But after solving the cubic equation, it is necessary to check whether the results are inside the physically meaningful range. (Of course, the problem can only occur at supercritical temperatures. Hence an alternative precaution would be to calculate the critical temperature and, if $T > T_c$, to retain the *largest* volume only. Either way, it is necessary to verify the physical validity of the solutions if there is more than one.)

Figures 1 and 2 also show the reason for the appearance of undesirable roots: cubic equations of state have up to three real poles, which divide the range of molar volumes into four domains (labeled I–IV in the diagrams). The highest pole is of first order and lies at $V_m = b$. The "real" domain I is at $V_m > b$. As shown in the diagram, the equation of state can have a branch with positive pressure values in domain III, and this can give rise to undesirable solutions.

The generalized cubic equation of state can be written as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2 + c_1 V_m + c_0} \tag{11}$$

where a usually is a function of temperature. In principle it is possible to cast this equation into a polynomial form 3 and to derive the conditions under which undesirable solutions appear from its discriminant. However, this leads to a rather cumbersome polynomial equation.

Instead of looking for the number of solutions, it is advantageous to locate the minimum of the equation of state in domain III. Physically unreasonable solutions can only occur at pressures above this minimum.

Again, the evaluation of the conditions of this minimum is tedious. It is possible, however, to treat the problem approximately by studying the function

$$h(V_m) = p(V_m - b) = RT - \frac{a(V_m - b)}{V_m^2 + c_1 V_m + c_0} \tag{12}$$

which is obtained from the equation of state by "multiplying out" the highest pole. The other poles—if they exist—remain unchanged, and it is safe to assume that the extrema of this function are close to those of the equation of state. Differentiation of this function with respect to V_m leads to

$$\frac{dh(V_m)}{dV_m} = -a \frac{-V_m^2 + c_0 + 2bV_m + c_1 b}{\left(V_m^2 + c_1 V_m + c_0\right)^2} \tag{13}$$

Thus, the existence of an extremum of $h(V_m)$ at $V_m < b$ requires that the numerator of Eq. 13 vanishes, and this leads to an equation for the molar volume of the extremum

$$V_{m,e} = b - \sqrt{b^2 + bc_1 + c_0} \tag{14}$$

It should be noted that this molar volume does not depend on temperature, unless the covolume parameter is made temperature-dependent.

Equation 14 can now be applied to some cubic equations of state

• For the equation of *van der Waals* we have $c_0 = c_1 = 0$; hence, the only extremum can occur at $V_m = 0$. However, the equation of state has a second-order pole at this molar volume, and so domain III has zero width. Therefore, the van der Waals equation does not produce physically unreasonable solutions for the molar volume.

• The *Redlich–Kwong equation* (Redlich and Kwong, 1949) is characterized by $c_0 = 0$ and $c_1 = b$. It has three poles, and the minimum in domain III is at $V_{m,e} = b(1 - \sqrt{2})$, which is a negative number. The pressure at this minimum is given by

$$p = \frac{RT}{-\sqrt{2}\,b} - \frac{a}{\left(4 - 3\sqrt{2}\right)b^2} \tag{15}$$

The contribution of the repulsive part of the equation of state is negative, and that of the attractive part positive. Since the repulsive part has a stronger temperature dependence ($\propto T$) than the attractive one ($a \propto 1/\sqrt{T}$ in the original version), increasing the temperature will generally lower the pressure above which physically unreasonable densities can be generated. In Figure 1 this pressure is extremely high. One should

not conclude, however, that these solutions have no practical importance: For hydrogen, the Redlich–Kwong equation yields multiple solutions at 600 K and 50 MPa, which is already in the range of technical hydrogenations.

• The *Peng–Robinson* equation (Peng and Robinson, 1976) is characterized by $c_1 = 2b$ and $c_0 = -b^2$. The situation is quite similar to the Redlich–Kwong equation; the minimum is even located at the same molar volume.

• The Trebble–Bishnoi–Salim equation (Salim and Trebble, 1991) has two additional substance-dependent parameters, c and d. The characteristic parameters of the generalized cubic equation are $c_1 = b + c$, $c_0 = -(bc + d^2)$, and $V_{m,e} = b(1 - \sqrt{2 - d^2/b^2})$. Hence, this equation can generate physically unreasonable solutions if $d < \sqrt{2}\,b$. The poles of the attractive term of this equation of state are further apart; hence, this equation of state is apt to produce physically unreasonable solutions, as is shown by Figure 2. For this equation the isotherm branch in domain III can even cross the abscissa, which means that physically unreasonable solutions can occur at *any* positive pressure.

New Algorithm

While the program code of Cardano's formula can be written in a rather compact way, it involves numerous references to "slow" functions, for example, higher-order roots and trigonometric functions, and it may therefore be worthwhile to look for alternatives. The following algorithm uses iteration, followed by deflation, to solve cubic equations.

Algorithm 2: New algorithms for solving cubic equations

Given is a polynomial equation with real coefficients a_i:

$$a_3 x^3 + a_2 x^2 + a_1 x + a_0 = 0 \qquad \text{with} \qquad a_3 \neq 0$$

1. Divide by a_3 to obtain the normalized form

$$x^3 + b_2 x^2 + b_1 x + b_0 = 0 \qquad \text{with} \qquad b_i = \frac{a_i}{a_3}$$

2. Determine an interval containing all real roots:

$$-r \leq x_k \leq +r \qquad \text{with} \qquad r = 1 + \max(|b_i|)$$

3. Select an initial value from the interval boundaries:

$$x^{(0)} = \begin{cases} -r & \text{if } g(x_{\text{infl}}) > 0 \\ +r & \text{if } g(x_{\text{infl}}) \leq 0 \end{cases}$$

where $x_{\text{infl}} = -1/3 b_2$ is the location of the inflection point. This choice ensures that no extremum lies between the initial value and the nearest root.

Table 1. CPU Time Required to Determine All Roots of a Cubic Polynomial

	$t/\mu s$	
Algorithm	1 Real Root	3 Real Roots
1 (Cardano)	2.0	3.5
2 (This work)	1.2–1.7	1.9–2.4

4. Iterate of the first root by Kepler's method:

$$x^{(k+1)} = x^{(k)} - \frac{g(x^{(k)}) g'(x^{(k)})}{\left[g'(x^{(k)})\right]^2 - \frac{1}{2} g(x^{(k)}) g''(x^{(k)})}$$

As no inflection points or extrema are lying between the initial value and the nearest root, as ensured by the previous step, convergence is guaranteed. This iteration scheme requires first and second derivatives. Care should be taken to minimize the number of multiplications within the iteration loop.

5. Perform a deflation (division of the nomalized cubic polynomial by a linear factor containing the first root, x_1):

$$c_2 = 1$$

$$h(x) = \sum_{i=0}^{2} c_i x^i \qquad \text{with} \qquad c_1 = c_2 x_1 + b_2$$

$$c_0 = c_1 x_1 + b_1$$

6. Find the roots (if any) of the quadratic polynomial $h(x)$ analytically.

Test runs on a workstation [Hewlett-Packard Series 9000/B1000 (processor HP-PA-RISC 8500, 300 MHz)] showed that Algorithm 2 is indeed faster than Cardano's formula, as shown by Table 1. Being mostly iterative, the new algorithm does not suffer from loss of accuracy as does Cardano's. (Algorithm 2 is a general solver for cubic polynomials; it does not exclude unphysical solutions. When it is applied to equations of state, it is necessary to check whether the solutions are physically meaningful).

Conclusion

With many cubic equations, the calculation of molar volumes for fixed pressure and temperature can produce physically unreasonable values, with $V_m < b$. Generally, one has to be on guard against such unwanted solutions when working with light gases (such as helium, hydrogen, nitrogen, methane) at high reduced temperatures. The tendency to develop such solutions is greater if the two lower poles of the equations of state are farther apart.

The existence of physically unreasonable solutions is not an argument against classic cubic equations; it is necessary, however, to make sure that such solutions are discarded within computer programs. The common programming practice to use the lowest root of a cubic equation as liquid volume can lead to erroneous results or premature program terminations.

Root calculation by Cardano's formula should always be followed with a Newton iteration step.

Cardano's method is not the fastest algorithm for finding the roots of a cubic polynomial.

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