Effective Utilization of Equations of State for Thermodynamic Properties in Process Simulation

Thermodynamic property computations using equations of state first require computation of the density root. Since higher level calculations such as single-stage flash, distillation and data regression are usually performed iteratively, properties are often demanded at conditions where the appropriate density root does not exist. A strategy of returning suitable pseudoproperties under such conditions is proposed. It has been successfully used in ASPEN (Advanced System for Process Engineering), a general process simulator developed at the Massachusetts Institute of Technology.

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SCOPE

In modern computer-aided process design, equations of state are being used increasingly to provide fugacity coefficients, enthalpies, entropies and densities of vapor and liquid mixtures, frequently at severe conditions. Equations such as the Soave modification of the Redlich-Kwong equation (Soave, 1972), the Peng-Robinson equation (Peng and Robinson, 1976), and the corresponding states correlation of Starling and coworkers (Brule et al., 1981) are capable of providing excellent results, even at difficult conditions such as the critical and retrograde regions.

Since the thermophysical properties system is at the lowest level of the computational hierarchy in a general process simulator, it is executed with the highest frequency. Robustness at this level is exceedingly important, but satisfying the demand for robustness is made more difficult by severe and varied operating conditions and the inevitable conflict with computational efficiency.

Higher level algorithms in process simulation, such as those for performing single-stage flash, multistage distillation or data regression calculations generally operate iteratively. During these iterative calculations, combinations of temperature, pressure and composition may occur that are infeasible according to the equation of state being used. The responsibility for robustness under these circumstances may be placed with either the higher level algorithm or the thermophysical properties system, i.e., the equation of state model. Previously two approaches to this problem have been suggested. Huron et al. (1978) and Asselineau et al. (1978) have changed the conditions at the higher level such that they are feasible. Poling et al. (1981) recommended that the equation of state model adjust the conditions in an appropriate manner to a feasible region, but the original conditions are retained for use at the higher level. Both approaches have deficiencies. In this work a strategy of returning suitably determined pseudoproperties at infeasible conditions is proposed. The new strategy allows less complicated higher level algorithms while at the same time increasing overall computational robustness and efficiency.

CONCLUSIONS AND SIGNIFICANCE

The implementation of robust process simulation algorithms using thermodynamic properties obtained from equation of state models for applications such as single-stage flash, distillation and data regression has become very important. Robustness of the simulation algorithms is made difficult by the complicated P-ρ-T-x topology of equations of state. But simulation algorithms are only concerned with the values of derived properties, principally enthalpy departure and fugacity coefficients, as a function of temperature, pressure and composition. This work proposes a strategy such that derived properties are calculated efficiently when they do exist and suitably determined pseudoproperties are returned when actual properties do not exist because of iterative excursions into infeasible regions.

The proposed strategy ensures that derived properties always vary in a reasonable manner, thereby promoting convergence of the flash, distillation and regression algorithms. Since these higher level algorithms are always assured of reasonable derived properties, they need not incorporate detailed knowledge of the complicated P-ρ-T-x topology of equations of state. The strategy has been found to be very effective in a wide range of applications using the ASPEN process simulator.

PROBLEM DESCRIPTION

Algorithms for solving single-stage flash and multistage separation tower problems utilize iterative procedures for the simultaneous solution of the phase equilibrium equations and the mass and enthalpy balances. Typically the temperature (or pressure) and composition of the vapor and/or liquid mixture change with each iteration. It is required that the equation of state (EOS) model supply values of the enthalpy departure Δh and/or fugacity coefficient ϕ at the given temperature, pressure and composition, and for a specified state (vapor or liquid). Since all useful equations of state are of the pressure explicit form:

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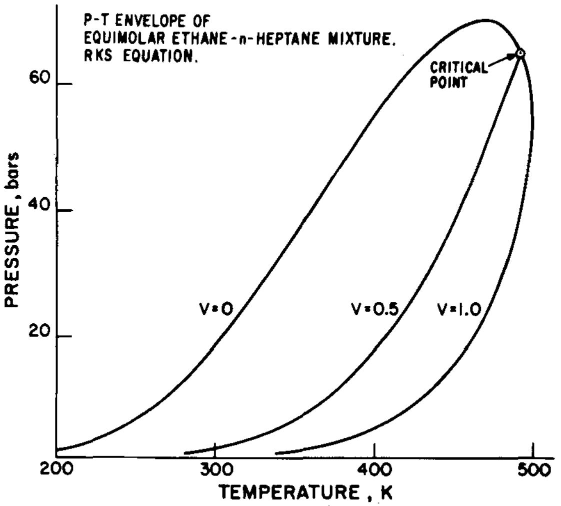

Figure 1. P-T envelope of equimolar ethane-n-heptane mixture using the Redlich-Kwong-Soave equation. It shows vapor fractions of 0.0 (bubble point), 0.5 and 1.0 (dew point).

$$P = g(T,\rho,x) \tag{1}$$

a solution for the molar density ρ is first required, and then Δh and ϕ may be calculated using standard thermodynamic relationships (Reid et al., 1977).

Determination of the density root of Eq. 1 is the first step in data regression applications as well as in phase equilibrium and heat and material balance calculations. For example, in the regression of VLE data, several calculations of vapor and liquid fugacity coefficients are performed at specified temperature, pressure and composition with varying values of the parameters to find values that best fit the data.

Since the density solution is performed frequently it must be efficient and robust. But more importantly, since higher level computations are nearly always iterative, properties are often demanded at infeasible conditions. The problem of infeasible specifications can be handled by either the higher level algorithm or the EOS model.

It does not seem appropriate for the higher level algorithm to handle the problem of infeasible specifications in a general purpose simulation system such as ASPEN with a wide range of models available, including those that are not based on equations of state. Approaches such as those proposed by Huron et al. (1978) and Asselineau et al. (1978) tend to result in unnecessary complexity, and could well interrupt orderly progress toward the solution. Further, different measures would probably be necessary for different models. A particularly difficult situation occurs in the case of data regression where infeasible specifications could result from changes in parameter values. Here it would be practically impossible for the regression algorithm to embody a sufficiently versatile and effective strategy to be both robust and efficient.

Thus it seems more effective for the EOS model to handle the problem. Poling et al. (1981) have proposed that the EOS model change appropriate specified variables such that the specification becomes feasible, but the original conditions are retained for use in the higher level computation. Although they report success with this approach, it would appear to reduce robustness by creating destabilizing discontinuities in the higher level algorithm.

We have devised an approach in which the EOS model handles infeasible specifications by returning suitably determined pseudoproperties which are continuous across the boundary of the feasible region. Thus the higher level algorithm does not perceive infeasible regions and orderly convergence can be obtained in spite of excursions into such regions. The approach has been extensively tested with the quasi-Newton distillation and single-stage flash algorithms of Boston and coworkers (1979, 1978) and the data regression algorithm of Britt and Luecke (1973). The approach is equally applicable to all EOS models, and may therefore be embodied in a general purpose subroutine addressed by all of the EOS models available in a simulation system.

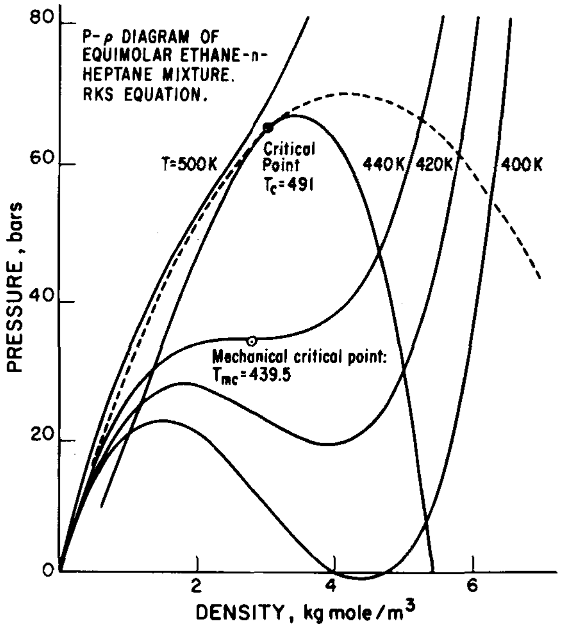

Figure 2. P-ρ diagram of an equimolar ethane-n-heptane mixture showing isotherms 500, 440, 420 and 400 K. It shows the equilibrium curve (dashed line) and the spinodal curve (full line). The critical point is the point at which the diffusional and spinodal curves meet tangentially. The mechanical critical point is defined by $\partial/\partial\rho|T = \partial^2P/\partial\rho^2|T = 0$.

DEVELOPMENT OF STRATEGY

To elucidate the problems encountered and the strategy we have adopted, we focus on the example of an equimolar enthane-n-heptane mixture modeled by a slightly modified version of the Redlich-Kwong-Soave equation (Soave, 1972 and Boston and Mathias, 1980). This example has been chosen only to demonstrate how the method works rather than to prove its superiority. The effectiveness of the method has been proved by its successful application in the widely used ASPEN process simulation system.

The P-T envelope of the mixture generated by the method of Chan and Boston (1981), Figure 1, shows retrograde behavior as described by many authors (e.g., Coward et al., 1978). Figure 2 shows a few pressure density (P-ρ) isotherms of the mixture and the equilibrium dome (dashed line) and the spinodal curve (full line) corresponding to incipient diffusional instability (Beegle et al., 1974). The equilibrium dome lies outside the diffusional dome and the two meet tangentially at the critical point.

Fluid conditions that lie within the spinodal dome are intrinsically unstable and hence cannot correspond to equilibrium points. At conditions between the spinodal and equilibrium domes the fluid is metastable. This means that while the fluid will not spontaneously split into two phases, a phase split will reduce the free energy and thus will occur. The point of interest here is that since higher level algorithms operate iteratively, because of poor initial guesses or temporary excursions fluid properties might be requested at conditions within the equilibrium dome or even the spinodal dome.

Another dome of interest is that corresponding to incipient mechanical instability. Although not shown in Figure 2, it can be visualized easily since it is the locus of points for which $P_\rho = (\partial P/\partial \rho)_{T,x} = 0$. At the top of this dome is the point at which the second derivative of pressure with respect to density is also equal to zero. For a pure fluid, this point is the critical point, but this is never so for a mixture (Rowlinson, 1979). In this paper, this point is referred to as the mechanical critical point, *mc*. It is important to note that the diffusional spinodal always lies outside the mechanical instability dome (Beegle et al., 1974).

The strategy we have developed for handling infeasible specifications draws on the points just discussed. Since a specification within the diffusional spinodal cannot correspond to an equilibrium point, the derived properties returned for such a specification need not correspond exactly to the equation of state, but can and should be those which will promote convergence of the higher level algorithm. This means that the continuity of the derived properties should be ensured for any excursion into the nonequilibrium region, and the trends as pressure or temperature change should in some sense be appropriate for the specified phase. Our strategy is to achieve this by adjusting the calculated properties in various ways, and returning values referred to as "pseudoproperties" to the higher level algorithms.

The effective implementation of this strategy requires an efficient and reliable means of recognizing the occurrence of infeasible specifications. In practice it is not feasible to explicitly determine the boundary of the unstable region. The location of a point on the diffusional spinodal requires finding the zero of the determinant of a matrix, whose order is the number of components in the mixture and whose elements are complicated functions. This calculation is much too expensive to be performed on a routine basis.

The approach that we have developed utilizes heuristics based only on the variation of pressure with molar density at constant temperature and composition to return true or pseudoproperties. The most conservative such heuristic would be to take the mechanical instability dome as the boundary inside of which to return pseudoproperties. A point on this dome is easily located at the root of the equation $P_\rho = 0$. The heuristic is too conservative, however, since problems can occur in the region just outside this dome. For instance, the vapor enthalpy departure changes too rapidly (Poling et al., 1981). Further, we have observed that the liquid-phase fugacity coefficients of light components go through nonphysical maxima. Thus we propose that pseudoproperties, having suitable trends and satisfying continuity conditions, be determined within some dome-shaped region just outside the mechanical instability dome. Following Poling et al. (1981), we propose a minimum value in P_ρ as the location of the boundary of this region. From empirical investigation it appears that a tenth of the product of the gas content and temperature is a good practical value for the allowed minimum of this derivative.

An unacceptable region, not covered by the minimum derivative criterion, could occur in the calculation of liquid properties at mechanically supercritical temperatures ($T > T_{cm}$) and low pressures. For example, for the enthane-n-heptane system, liquid properties might be requested at 500 K and 10 bar (Figure 2). In such cases, return of true properties would make the liquid phase appear "vapor-like" and might cause convergence to the trivial solution or even divergence in the higher level algorithm. In this regard, a fortunate observation, based on data from many systems modeled by several different equations of state, is that the true critical density is slightly greater than the mechanical critical density (Figure 2). Thus, for the liquid phase, we propose that pseudoproperties be returned when the liquid density is less than ρ_{mc}.

IMPLEMENTATION OF STRATEGY

Our approach for implementing the strategy just described is simple but effective. For specifications in the allowed region, the density root and corresponding derived quantities will be calculated efficiently. The criteria for the allowed region are:

$$P_\rho > P_\rho^* = 0.1\,RT \text{ (liquid and vapor)} \qquad (2)$$

$$\rho > \rho_{mc} \text{ (liquid only)} \qquad (3)$$

For specifications in the nonallowed region the aim is to provide derived properties that are continuous and have trends that are appropriate for the phase specified. Our approach is designed primarily to service quasi-Newton higher level algorithms which do not require explicit derivatives. [It is anticipated that a similar approach will be effective for Newton algorithms like that of Asselineau (1978) which require composition derivatives from the equation of state model.] Thus it is sufficient to ensure continuity and only small discontinuities, if any, in first derivatives for excursions across the boundary of the allowed region.

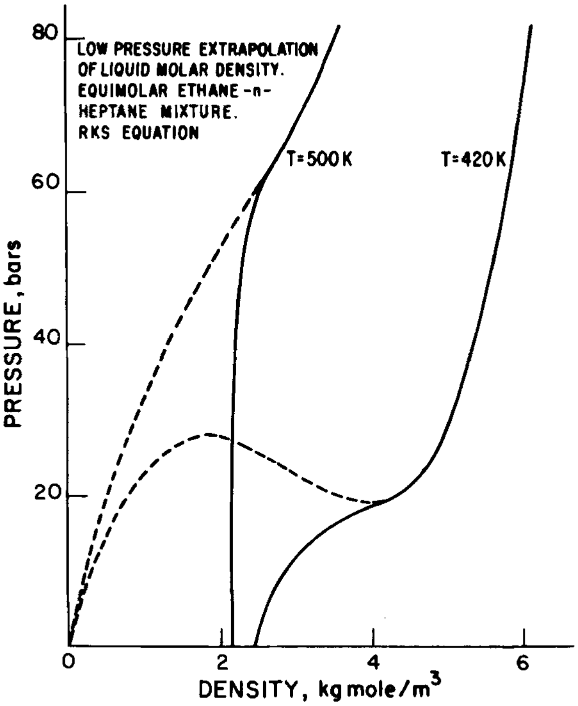

Figure 3. Low-pressure extrapolation of liquid molar density into the nonequilibrium region. The full line shows the P-ρ isotherm assumed by the model and the dashed line shows the actual P-ρ isotherm.

For the liquid phase we propose a logarithmic extrapolation of the form:

$$P = C_o + C_1 \ln(\rho - 0.7\,\rho_{mc}) \qquad (4)$$

The constants C_o and C_1 are determined by matching P and P_ρ at the boundary of the allowed region. Note that $P \rightarrow -\infty$ as $\rho \rightarrow 0.7\,\rho_{mc}$, a characteristic of Eq. 4 that results in smooth and physically reasonable extrapolations under all conditions. Examples of the liquid density extrapolation are shown in Figure 3.

For the vapor phase we propose a quadratic extrapolation of the reciprocal of pressure with density ensuring zeroth- and first-order continuity at the boundary of the allowed region, and imposing the condition $1/P = 0$ when $\rho = (\rho^* + \rho_{mc})/2$, where ρ^* is the value of ρ at the boundary of the allowed region. The reason for limiting the vapor density to a value less than ρ_{mc} is that the pressure can otherwise become negative at low reduced temperatures. Vapor density extrapolation is shown graphically in Figure 4.

Properties are then calculated at the density obtained by extrapolating to the specified pressure. The single exception to this is liquid-phase fugacity coefficients where it was found necessary to correct for the difference between the calculated and specified pressure:

$$\phi_i = \phi_i^{\text{calc}} \frac{P^{\text{calc}}}{P^{\text{spec}}} \qquad (5)$$

The difference between P^{calc} and P^{spec} may be illustrated by referring to Figure 3, which shows that $P^{\text{calc}} = 21$ bar when $T = 420$ K and $P^{\text{spec}} = 10$ bar.

Equation 5 requires further discussion. An important feature of our method is to creatively "invent" properties in the infeasible region. This is permitted since the pseudoproperties are used only as intermediate values in an iterative process. Furthermore, we contend that appropriately devised pseudoproperties are an aid to convergence. We found it was effective to invent properties which are continuous up to first order and maintain the correct trend with temperature and pressure. In general, properties cal-

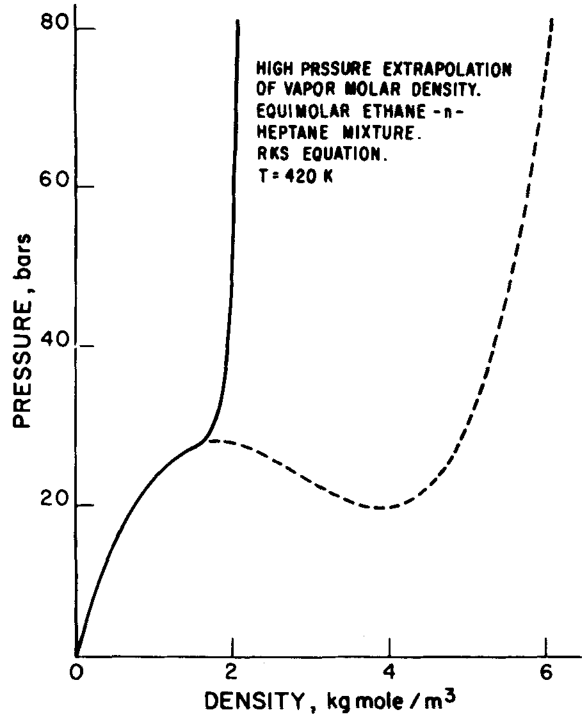

Figure 4. High-pressure extrapolation of vapor molar density into the nonequilibrium region. The full line shows the P-ρ isotherm assumed by the model and the dashed line shows the actual P-ρ isotherm.

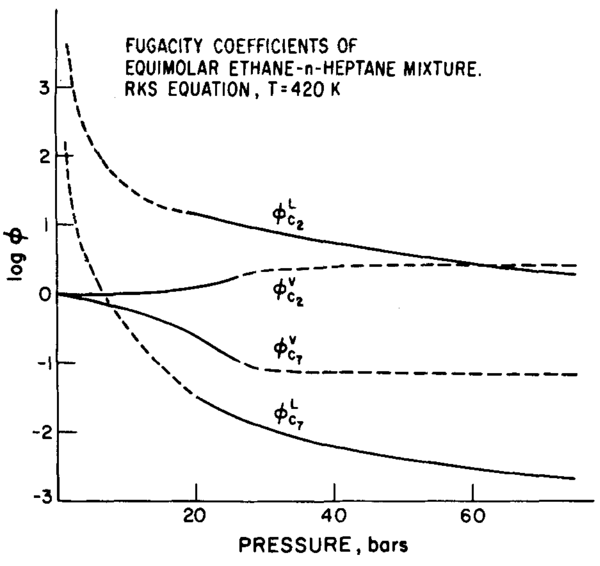

Figure 5. Fugacity coefficients of equimolar ethane-n-haptane mixture at 420 K. The dashed line shows pseudofugacity coefficients returned in nonequilibrium region.

culated at the pseudodensity achieve this goal. However, in the case of liquid fugacity coefficients, the values were found not to increase sufficiently rapidly with decreasing pressure, hence the correction provided by Eq. 5 improves the behavior. The correction was not applied to vapor fugacity coefficients because it causes them to decrease too rapidly with increasing pressure, creating the possibility of a false solution in the infeasible region (Figure 5).

Fugacity coefficients calculated by the proposed method are shown in Figures 5 and 6. Notice that the extrapolated values appear continuous with true values and maintain the correct trends.

Enthalpy departures are shown in Figure 7. Again continuity into the extrapolated region is maintained. Further, for the isotherm at 420 K, a reasonable "enthalpy of vaporization" is computed at all pressures including the very low and very high regions.

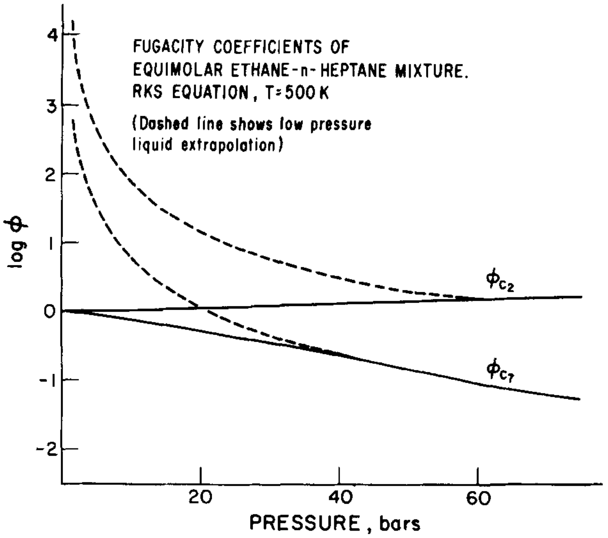

Figure 6. Fugacity coefficients of equimolar ethane-n-heptane mixture at a mechanically supercritical temperature (T = 500 K). The dashed line shows pseudofugacity coefficients returned for the low-pressure nonequilibrium region (liquid phase only).

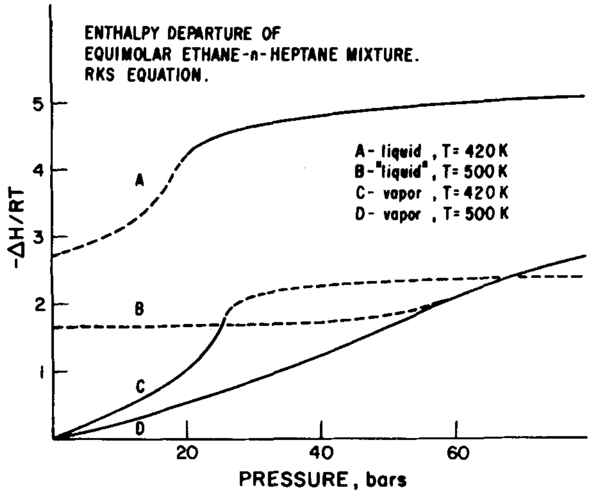

Figure 7. Enthalpy departure of equimolar ethane-n-heptane mixture. The dashed lines show pseudoenthalpy departures returned in the nonequilibrium region.

For the 500 K isotherm a pseudoenthalpy of vaporization is predicted at low pressure. We have found this behavior to be useful for flash and distillation algorithm convergence.

The approach described has been used successfully in the ASPEN process simulation system. It neither helps nor is a liability very close to the mixture critical point, but in all other regions it greatly aids process computations.

DENSITY ROOT CALCULATION

In the allowed region the molar density must be computed, and the boundary of the nonallowed region must be detected so that extrapolations, if necessary, can be performed. All this must be done efficiently and robustly. We have designed an iterative procedure to accomplish this task. The iterative procedure is employed for all equation of state models, including those where the density solution can be performed analytically. This perhaps requires justification.

Equations such as Redlich-Kwong-Soave (1972) and Peng-Robinson (1976) are referred to as "cubic" since the form of Eq. 1 can be transformed by the substitution $Z = P/\rho RT$ into the form

$$f(Z;T,P,x) = 0 \qquad (6)$$

where f is cubic in Z and thus can be solved analytically. It is generally recognized that an important advantage of the so-called cubic equations is that the density root calculation can be performed analytically. But at the same time there is agreement that the computed density root must be evaluated to determine whether it is in some allowed region (Coward et al., 1978; Mills et al., 1980; Poling et al., 1981). Thus additional calculations are required when the root is determined using the analytical solution. Our procedure does both computation and evaluation simultaneously and we contend that it is at least as efficient as analytical approaches for density calculations only, while being more efficient in cases where both calculation and evaluation are necessary. Further, it is applicable to equations of state which do not have analytical solutions, for example the BWR equation of Starling and coworkers (Brule, 1981).

The algorithm for liquid density calculation is first discussed. It begins with estimated values of the mechanical critical density ρ_{mc} and a limiting density ρ_o based on the particular equation of state being used. These quantities are readily available. For example for the Redlich-Kwong-Soave equation

$$\rho_o = 1/b \qquad (7)$$

$$\rho_{mc} = 0.2599/b \qquad (8)$$

where b is the hard core volume. For all other equations these quantities can be easily estimated. We note that exact values of these quantities are not essential.

The algorithm first finds a density between ρ_o and ρ_{mc} where $P^{calc} > P^{spec}$ and $P_\rho > P_\rho^*$. The initial estimate is obtained as:

$$\rho = \rho_o - 0.4\,(\rho_o - \rho_{mc}) \qquad (9)$$

This is sufficiently high to avoid the problems due to the multiple sigmoid sections observed by Mills et al. (1980) in the BWR equation. Next a second point is found at which $P_\rho > P_\rho^*$. The algorithm makes the valid assumption that the P-ρ isotherm is convex in the *allowed region*. Now if at the second point, the calculated pressure is less than P^{spec}, a Newton iteration procedure starting from the first point is guaranteed to converge to a solution in the allowed region. If at the second point $P^{calc} > P^{spec}$, a Newton iteration procedure is still used but the values of P_ρ at the last two points are used to find an estimate of ρ at which $P_\rho = P_\rho^*$, and this is used as a lower bound on ρ. As the Newton iteration continues, this bound changes. Hence it may be thought of as a moving lower bound. It quickly converges to either the solution or the boundary of the nonallowed region. Because of convexity, overshoot does not occur for mechanically subcritical temperatures ($T < T_{mc}$).

For mechanically supercritical temperatures we propose a simple secant calculation with the allowed region defined as $\rho > \rho_{mc}$ (Eq. 3). T_{mc} can be calculated exactly for the cubic equations. For the Redlich-Kwong-Soave (1972) equation

$$T_{mc} = 0.20268\, a/Rb \qquad (10)$$

where a is the attractive term in the equation. For other equations, mechanically supercritical conditions are detected when a maximum of the partial derivative of pressure with respect to volume occurs between successive iterations.

The algorithm for the vapor phase is analogous. When a specification in the nonallowed region is detected, its density root is calculated from the extrapolated equation described above.

After extensive testing we have found that the ASPEN implementation of the algorithm for determining the density root is reliable and efficient, normally converging within three to eight calls to the model to evaluate P^{calc} and P_ρ.

ACKNOWLEDGMENT

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NOTATION

a = attractive constant in Redlich-Kwong-Soave equation
b = hard core volume in Redlich-Kwong-Soave equation
C_o = constant in Eq. 4
C_1 = constant in Eq. 4
P = pressure
R = gas constant
T = temperature
x = mole fraction
V = vapor fraction
Z = compressibility factor
ρ = molar density
Δh = enthalpy departure
ϕ_i = fugacity coefficient of component i

Subscripts

c = critical property
mc = mechanical critical property
ρ = derivative with respect to molar density
o = limiting value

Superscripts

$*$ = limiting value
spec = specified by higher level algorithm
calc = calculated by equation of state model

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