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COMPUTATIONAL ASPECTS OF A NON-CUBIC EQUATION OF STATE FOR PHASE-EQUILIBRIUM CALCULATIONS. EFFECT OF DENSITY-DEPENDENT MIXING RULE

R.J. Topliss, D. Dimitrelis, and J.M. Prausnitz

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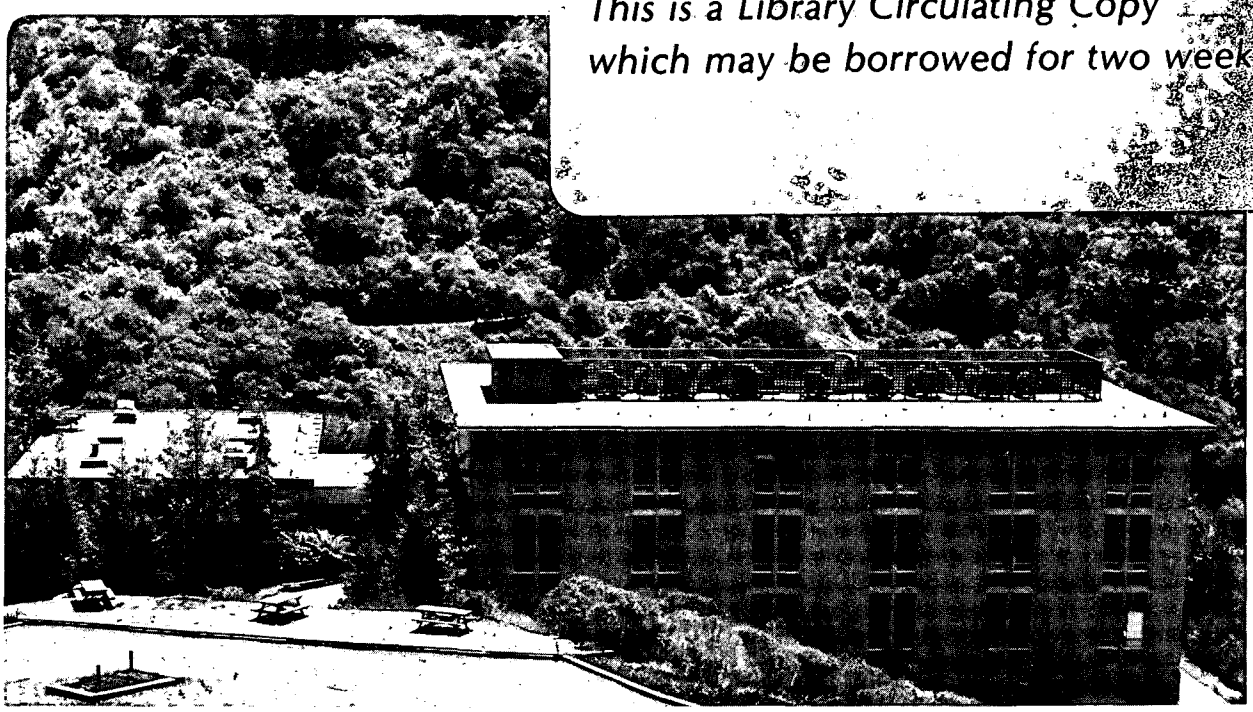

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COMPUTATIONAL ASPECTS OF A NON-CUBIC EQUATION OF STATE FOR PHASE-EQUILIBRIUM CALCULATIONS. EFFECT OF DENSITY-DEPENDENT MIXING RULES

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ABSTRACT

An efficient procedure is presented for solving a non-cubic equation of state for density. In phase-equilibrium calculations, the costly computing step is not the density calculation but the calculation of the equation-of-state constants for the mixture. Illustrative calculations are given for high-pressure phase equilibria for hydrogen/ethane and methane/water. These calculations show the superiority of non-cubic equations with density-dependent mixing rules.

SCOPE

Semi-theoretical equations of state provide molecular-thermodynamic models for computer-aided design of separation processes. However, cubic equations of state such as the Redlich-Kwong or the Peng-Robinson equation are not able to represent high-pressure phase equilibria of complex mixtures, e.g. hydrogen/solvent (Chokappa et al., 1985) or water/hydrocarbon mixtures (Peng and Robinson, 1980) over wide ranges of pressure, temperature and composition. In recent years, non-cubic equations with density-dependent mixing rules have been proposed to correlate highly asymmetric phase behavior (See for example, Mathias and Copeman, 1983; Lüdecke and Prausnitz, 1985; Mollerup, 1985; and Panagiotopoulos and Reid, 1986).

We address two questions concerning the use of non-cubic equations in phase-equilibrium calculations. The first relates to calculation of density from a pressure-explicit equation of state at a specified pressure, temperature and composition. A cubic equation can be solved analytically (Poling et al., 1981). A non-cubic equation must be solved iteratively (Mathias et al., 1984). During phase-equilibrium calculations combinations of pressure, temperature and composition may arise for which there is no valid density root according to the equation of state used. To discern what a density-finding procedure can and cannot do to identify thermodynamically unstable or inconsistent conditions, we examine how pressure varies with density at constant temperature and composition.

The second question concerns the computing time required to solve a non-cubic equation iteratively for density versus the time required to solve a cubic equation analytically. As shown by Mathias and Benson (1985), iterative calculations do not significantly increase overall computing time for solving the phase-equilibrium problem. We study the effect of increasingly complex mixing rules for the equation-of-state parameters on the computing-time requirements for finding density and for calculating fugacity coefficients in a multicomponent system. We consider the following cases: van der Waals-1 mixing rules for both the reference and the perturbation term of an equation of state; density-dependent mixing rules for the reference system and van der Waals-1 mixing rules for the perturbation term; and finally, density-dependent mixing rules for both reference and perturbation terms.

CONCLUSIONS AND SIGNIFICANCE

We present an efficient procedure to solve a pressure-explicit non-cubic equation of state for density. Our density-finding procedure converges reliably for difficult cases (e.g., roots in the pseudo-critical region); further, it handles the easier cases efficiently, needing no more than 5-7 iterations for convergence. In addition to solving for the roots of the equation of state, our procedure identifies inconsistent ("wrong-root") specifications.

We show that the most time-consuming step in phase-equilibrium calculations is the calculation of equation-of-state constants for the mixture (i.e., the mixing rules) and not the density calculation. This is particularly true for multicomponent mixtures as encountered in industrial applications. Rising complexity of the mixing rules increases significantly the computing time required to perform phase-equilibrium calculations.

We demonstrate the advantages of non-cubic equations with density-dependent mixing rules by presenting examples for high-pressure phase equilibria. Results are given for binary vapor-liquid equilibria of hydrogen/ethane and methane/water over a wide range of pressure, temperature and composition. Equations of state with density-dependent mixing rules correlate phase behavior for such highly asymmetric mixtures significantly better than equations with classical mixing rules.

INTRODUCTION

For computer-aided design of separation processes, thermodynamic properties are often needed over a wide range of conditions. Therefore, equations of state (EOS) are extensively used in phase-equilibrium calculations.

When two phases α and β are in equilibrium,

$$T^{\alpha} = T^{\beta} \tag{1}$$

$$P^{\alpha} = P^{\beta} \tag{2}$$

$$x_i^{\alpha}\phi_i^{\alpha}(P,T,\underline{x}^{\alpha}) = x_i^{\beta}\phi_i^{\beta}(P,T,\underline{x}^{\beta}) \qquad i = 1,2,\ldots,m \tag{3}$$

where T is temperature, P is pressure, $\underline{x}$ is mole fractions, x_i is mole fraction of component i and m is number of components.

The fugacity coefficient ϕ_i of component i at pressure P, temperature T and composition $\underline{x}$ is calculated from a pressure-explicit EOS according to

$$\ln\phi_i(P,T,\underline{x}) = \int_0^{\rho}\left\{\frac{1}{\rho^2 RT}\left[\left(\frac{\partial(NP)}{\partial n_i}\right)_{\rho,T,n_{\neq i}} - \rho RT\right]\right\} d\rho + \left(\frac{P}{\rho RT} - 1\right) - \ln\frac{P}{\rho RT} \tag{4}$$

where R is the universal gas constant, N is total number of moles and n_i is number of moles of component i. To evaluate the fugacity coefficient, it is necessary to know the molar density ρ corresponding to pressure P, temperature T and composition $\underline{x}$ for the phase of interest. It can be calculated from a pressure-explicit EOS.

When solving an EOS for density, it is convenient to think of the $P(\rho,T,\underline{x})$ hypersurface as a family of $P(\rho)$ curves. For a given set of specified conditions $(P^s,T^s,\underline{x}^s)$, a specific $P(\rho)$ curve is determined by $(T^s,\underline{x}^s)$; the corresponding density is found by solving the implicit equation

$$P(\rho) \equiv P(\rho, T = T^s, \underline{x} = \underline{x}^s) = P^s \tag{5}$$

where superscipt s denotes specified. Solution of eqn. (5) constitutes the first step in evaluation of thermodynamic properties from an EOS when $(P,T,\underline{x})$ are specified. We refer to a computational procedure that performs this task as a density-finding procedure.

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In recent years, non-cubic EOS with density-dependent mixing rules have been proposed to correlate highly asymmetric phase behavior. For a cubic EOS, $P(\rho)=P^s$ can be rearranged into a third-degree polynomial and solved analytically. For a non-cubic EOS, we require an iterative density-finding procedure. In addition to solving a non-linear equation for a specific root, a density-finding procedure should participate in identifying inconsistent specifications. We say "participate" because a density-finding procedure by itself, which only has access to $P(\rho)$ information, cannot always identify conditions where there is no thermodynamically stable phase or where the only stable phase is not the phase of interest.

DENSITY-FINDING PROCEDURE

Figure 1 schematically illustrates the task of a density-finding procedure. Specifying the temperature T^s and composition $\underline{x}^s$, the EOS parameters for the mixture (i.e., the mixing rules) are calculated and the pressure-explicit EOS is reduced to an expression for $P(\rho)$. The density-finding procedure has to solve this expression for the density ρ corresponding to the specified pressure P^s and phase of interest. If there is more than one real root of $P(\rho)=P^s$ in the valid range of density, the smallest root corresponds to a vapor phase, and the largest to a liquid phase. If there is only one real root, it may correspond to a vapor, liquid, or supercritical-fluid phase. Therefore the density-finding procedure must return the density ρ, a classification of the $P(\rho)$ curve and a classification of the density.

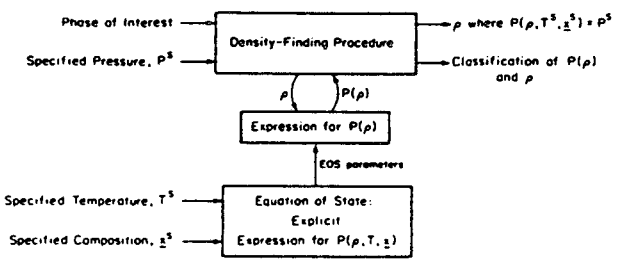

Fig. 1. Purpose and operation of a density-finding procedure.

To illustrate some of the possible locations for equilibrium roots for a multicomponent system, we present predicted vapor-liquid equilibria for the methane/propane system at 300 K using the Carnahan-Starling/van der Waals (CSW) equation (Dimitrelis and Prausnitz, 1986). Figure 2(a) shows the equilibrium envelope on a pressure-composition diagram with the critical point, the pseudo-critical point[1] and the equilibrium pressures for three indicated compositions. The $P(\rho)$ curves for these compositions are shown in Figure 2(b) with the corresponding points indicated. The curves behave similarly in the limits of low and high density. All of the curves display ideal-gas behavior in the limit of $\rho=0$ (i.e., $P=0$ and $dP/d\rho=RT$), and $P(\rho)$ and $dP/d\rho$ have large, positive values in the limit of closed-packed density. However, the curves have different features between these extremes.

The curve with methane mole fraction of 0.3 has a local maximum and a local minimum; it has one or three real roots depending on the specified pressure P^s. Densities less than that for the maximum in $P(\rho)$ correspond to a vapor phase, and densities greater than that for the minimum correspond to a liquid phase.

The other curves are monotonic; they have only one real root for any P^s. Both liquid and vapor roots can lie on such curves. It is also apparent that vapor roots can lie on either side of the inflection in $P(\rho)$ and on either side of the pseudo-critical density.

Figure 3(a) presents schematically the basic types of $P(\rho)$ curves discussed above; the corresponding $dP/d\rho$ curves are indicated in Figure 3(b). (Curve C is similar to curve B with the exception of not exhibiting a point of inflection; this is typical for temperatures above the Boyle[2] temperature.)

The only input required by our density-finding procedure, other than the specified conditions, is the density ρ_{lim} where $P(\rho)$ goes to infinity (ρ_{lim} is an EOS-specific parameter). Our density-finding procedure first establishes upper and lower bounds on a range of density that includes all physically meaningful roots. The lower bound ρ_{lb} is set to zero. The upper bound ρ_{ub} is established by stepping carefully from $0.4\rho_{lim}$ toward ρ_{lim} until a suitable value for ρ_{ub} is found, such that

$$\left[\frac{dP}{d\rho}\right]_{\rho=\rho_{ub}} > 0 \text{ and } P(\rho_{ub}) > P^s \tag{6}$$

Then it performs two iterative calculations that classify $P(\rho)$ and determine whether the desired root exists. If it exists, the desired root has been isolated, and a third calculation solves $P(\rho)=P^s$. Our three-stage procedure is reliable because each iterative calculation operates in a bounded range of density that has one and only one zero for the function to be solved. It performs efficiently over the entire range of specified conditions by taking advantage of the mathematical nature of $P(\rho)$ and by using iterative techniques based on quadratic approximations over bounded regions.

Our density-finding procedure assumes that $P(\rho=0)=0$ and $(dP/d\rho)_{\rho=0}=RT$; an EOS that violates these ideal-gas limits is inappropriate for modelling vapor phases. Further, it assumes that $dP/d\rho$ has at most one minimum and no maximum in the bounded range. That is, $dP/d\rho$ increases monotonically from RT to $(dP/d\rho)_{\rho=\rho_{ub}}$, or it decreases to a minimum before increasing to $(dP/d\rho)_{\rho=\rho_{ub}}$. Most EOS yield $P(\rho)$ curves that conform to these restrictions, but some EOS of an empirical nature (e.g., the Benedict-Webb-Rubin EOS (Benedict et al., 1940)) display more complicated behavior, especially at low temperatures. Density-finding procedures for these EOS (Mills et al., 1980) must take special precaution to insure reliability that make them inefficient for general applications. Finally, it is assumed that a subroutine is available to evaluate $P(\rho)$ and $dP/d\rho$.

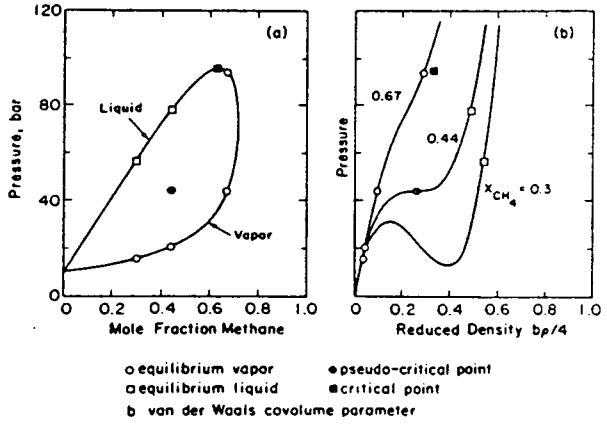

Fig. 2. Predicted vapor-liquid equilibria for methane/propane at 300 K using the Carnahan-Starling/van der Waals equation ($k_{CH_4C_3H_8}=0$).
[(a) $P-x$ diagram; (b) $P-\rho$ diagram]

We now describe schematically the computational algorithm for solving an EOS for density. In a preliminary calculation, our density-finding procedure first evaluates $dP/d\rho$ at $\rho=0.0001\rho_{lim}$ to approximate $(d^2P/d\rho^2)_{\rho=0}$. If $(d^2P/d\rho^2)_{\rho=0}>0$, there is no minimum in $dP/d\rho$ (type-C curve); thus, the desired root has been isolated in a range where $P(\rho)$ is monotonic, and the procedure branches to the third stage which finds the root. If $(d^2P/d\rho^2)_{\rho=0}<0$, there is a minimum in $dP/d\rho$ (type-A or type-B curve), and the procedure enters the first stage which finds ρ_{inf}, the density for the inflection in $P(\rho)$ (minimum in $dP/d\rho$).

[1] For a given composition $\underline{x}^s$, there is a temperature T^s that yields a $P(\rho)$ curve containing a point where $dP/d\rho=d^2P/d\rho^2=0$ which is called the pseudo-critical point. This is not the critical point for the mixture.

[2] For a given composition $\underline{x}^s$, there is a temperature T^s such that $(d^2P/d\rho^2)_{\rho=0}=0$. This is called the Boyle temperature.

The sign of $(dP/d\rho)_{\rho=\rho_{inf}}$ indicates whether $P(\rho)$ contains no or two extrema in the bounded range. If $(dP/d\rho)_{\rho=\rho_{inf}}>0$, $P(\rho)$ contains an inflection but no extrema (type-B curve); thus, the desired root has been isolated in a range where $P(\rho)$ is monotonic, and the procedure branches to the third stage which finds the root. If $(dP/d\rho)_{\rho=\rho_{inf}}<0$, $P(\rho)$ contains a maximum and a minimum (type-A curve). In addition to distinguishing between type-A and type-B curves, finding ρ_{inf} isolates the zeros of $dP/d\rho$ for type-A curves. The low-density zero (maximum in $P(\rho)$) is located between ρ_{lb} and ρ_{inf}, and the high-density zero (minimum in $P(\rho)$) is located between ρ_{inf} and ρ_{ub}. Depending on the phase of interest, the procedure resets the appropriate bound before entering the second stage which finds ρ_{ext}, the density for the extremum in $P(\rho)$ (zero of $dP/d\rho$).

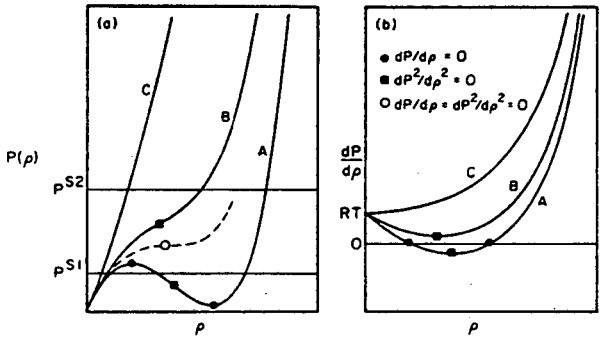

Fig. 3. The three basic types of $P(\rho)$ curves and the corresponding $dP/d\rho$ curves.

After finding ρ_{ext}, $P(\rho_{ext})$ is compared with P^s to determine whether there is a root for the phase of interest. If $P(\rho_{ext})<P^s$ for a vapor phase (as when $P^s=P^{s2}$ in Figure 3(a)) or $P(\rho_{ext})>P^s$ for a liquid phase, there is no root for the phase of interest at the specified conditions (the only root is the wrong root), and the procedure terminates. If the desired root exists, the appropriate bound is reset to ρ_{ext} before entering the third stage.

The purpose of the first three calculations (the preliminary calculation and the first two stages) is to classify the $P(\rho)$ curve and to establish bounds for the third stage which finds ρ_{des}, the desired root of $P(\rho)=P^s$. Regardless of the type of curve, upon entering the third stage, the desired root is isolated in a range $\rho_{lb}<\rho_{des}<\rho_{ub}$ where $P(\rho)$ is monotonically increasing. To find ρ_{des} in the bounded range, we use an iterative technique based on a quadratic approximation of $P(\rho)$. Even in the vicinity of double roots, it gives high-order convergence. Convergence is typically achieved in a total of 5-7 iterations.

Our density-finding procedure can characterize a $P(\rho)$ curve according to its features and classify the roots for a type-A curve; but it cannot identify other types of inconsistent specifications. Various authors (most notably Poling et al., 1981, and Mathias et al., 1984) have proposed heuristics to identify roots violating material-stability criteria and mechanically stable roots not corresponding to the phase of interest ("wrong roots"). However, heuristics may be inappropriate within a density-finding routine; they can exclude valid roots in the near-critical region (Topliss, 1985), an important region in phase-equilibrium calculations for some separation processes such as supercritical-fluid extraction. Such heuristics may be useful in higher level procedures to decide whether or not rigorous stability analysis is warranted. If a root is found that violates the heuristics, then the routine that calculates the fugacity coefficients could also calculate their composition derivatives, and the rigorous criteria for material stability could be evaluated (Michelsen, 1982a, and Topliss, 1985). Our density-finding procedure excludes only wrong roots on type-A curves and roots violating the mechanical-stability criterion, i.e. roots where $dP/d\rho$ is negative.

One common misconception has been that the iterative density-finding procedure consumes the majority of the time needed to calculate the thermodynamic properties required for solving the phase-equilibrium problem [eqns. (1)-(3)]. However, as shown in the next section, the time for the density calculation is only a small fraction of the total time required for calculation of thermodynamic properties.

COMPUTING-TIME STUDIES

Figure 4 shows CPU times for phase-equlibrium calculations for the Carnahan-Starling/van der Waals equation of state (CSW EOS) (Dimitrelis and Prausnitz, 1986) as a function of the number of components in the mixture.[3] We present incremental CPU times for calculating first the EOS parameters at specified temperature T^s and composition $\underline{x}^s$; for solving the equation $P(\rho)=P^s$; for calculating subsequently the fugacity coefficients; and finally, for calculating analytically the derivatives of the fugacity coefficients with respect to pressure and composition (Topliss, 1985). The CPU times are normalized by the time required to calculate the EOS parameters for the CSW EOS and to solve for density for a binary mixture. The CPU times are obtained by performing a particular calculation many times to obtain a reliable average.

Computing time for calculating the EOS parameters dominates the overall CPU-time requirements, particularly for multicomponent mixtures. The overall cost of solving an EOS for density is not sensitive to the number of $P(\rho)$ evaluations when the number is small. (In these examples the density-finding procedure needs 7 iterations to converge.) Increasing the number of $P(\rho)$ evaluations by one for an eight-component mixture results in only a 5% increase in the overall CPU time required to solve for density. Consequently, for mixtures with a large number of components, reliability of the density-finding procedure is more important than efficiency.[4]

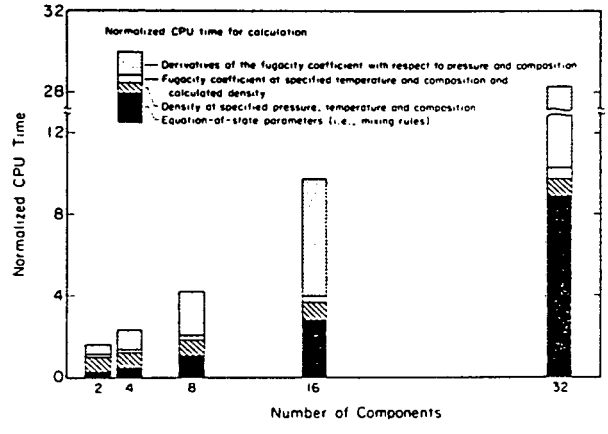

Fig. 4. CPU time for phase-equilibrium calculations as a function of the number of components for the Carnahan-Starling/van der Waals equation.

The incremental cost for calculating the fugacity coefficients is about 10% regardless of the number of components. The incremental cost of analytically calculating the m pressure derivatives and the $m\times m$ matrix of the composition derivatives is never more than twice the overall cost of calculating the fugacity coefficients (Michelsen, 1982b, and Michelsen and Mollerup, 1986). By comparison, calculating the composition derivatives by finite-difference approximations requires m evaluations of the fugacity coefficients and solution of a set of $m-1$ linear equations. These derivatives are needed for material-stability analysis (Michelsen, 1982a) and for calculations in the near-critical region (Michelsen, 1980).

Having identified computation of the EOS parameters as the most time-consuming step in phase-equilibrium calculations, we study next the effect of increasingly complex mixing rules on

[3] To avoid unnecessary nested summations, we express the mixing rule for van der Waals covolume parameter b by

$$b=\sum_{i=1}^{m}\sum_{j=1}^{m}x_ix_j\left[\frac{b_i^{1/3}+b_j^{1/3}}{2}\right]^3=\frac{\sum_{i=1}^{m}x_ib_i+3\sum_{i=1}^{m}x_ib_i^{2/3}\sum_{i=1}^{m}x_ib_i^{1/3}}{4} \tag{7}$$

[4] This is not valid for an EOS where calculation of the EOS parameters cannot be separated from the density dependence; e.g., for an EOS with local-composition mixing rules (Whiting, 1982, and Topliss et al., 1982). Such EOS are more expensive to use and the overall cost is more sensitive to the number of $P(\rho)$ evaluations required to solve for density.

the overall computing time required to calculate fugacity coefficients. To facilitate comparison, we use throughout the same molecular-thermodynamic model: an EOS with a hard-sphere reference system and a van der Waals perturbation term.

We consider four cases: the Carnahan-Starling/van der Waals equation (CSW EOS) with van der Waals-1 mixing rules for both the reference and the perturbation terms (Dimitrelis and Prausnitz, 1986); the Boublik-Mansoori/van der Waals equation (BMW EOS) (Dimitrelis and Prausnitz, 1986), with density-dependent mixing rules for the reference term[5] and van der Waals-1 mixing rules for the perturbation term; the Boublik-Mansoori/van der Waals equation with second-virial correction (BMW/SV EOS) (Dimitrelis and Prausnitz, 1987) with density-dependent mixing rules for both reference and perturbation terms; and finally, the Boublik-Mansoori/van der Waals equation with second-virial correction and cubic mixing rule for attractive-force parameter a (BMW/SV+x^3 EOS) (Dimitrelis and Prausnitz, 1987) with density-dependent mixing rules for both reference and perturbation terms.

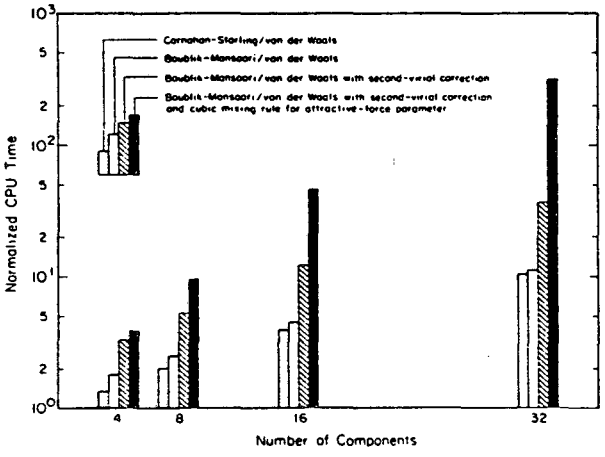

Fig. 5. CPU time for fugacity-coefficient calculation as a function of the number of components for equations with increasingly complex mixing rules.

Figure 5 shows normalized CPU times for calculating the fugacity coefficient as a function of the number of components. (Note the logarithmic scale on the vertical axis.) The CPU times are normalized as in Figure 4. To simplify comparison, we use for all EOS the same temperature dependence for van der Waals covolume parameter b

$$b_i = \frac{RT_{c,i}}{P_{c,i}} \frac{b_i^{(0)} + b_i^{(1)} T_{r,i}^2}{1 + b_i^{(2)} T_{r,i}^2} \tag{8}$$

and for attractive-force parameter a

$$a_i = \frac{(RT_{c,i})^2}{P_{c,i}} \frac{a_i^{(0)} + a_i^{(1)} T_{r,i}^2}{1 + a_i^{(2)} T_{r,i}^2} \tag{9}$$

Subscript c refers to the critical point and reduced temperature $T_r = T/T_c$.

The BMW EOS consumes slightly more CPU time than the CSW EOS. The computer implementation of these EOS contains the same number and type of summations involving component mole fractions. They require three summations, linear in mole fraction, for the calculation of van der Waals covolume parameter b [right-hand side of eqn. (7)] in the reference term and one summation, quadratic in mole fraction, for the calculation of attractive-force parameter a [eqn (11)]. The reference term of the BMW EOS has a slightly more complicated algebraic form than that of the CSW EOS (Dimitrelis and Prausnitz, 1986).

Because of two additional quadratic-mole-fraction summations, the BMW/SV EOS consumes about three times more CPU time than the BMW EOS. The additional summations are required for the calculation of the second virial coefficient (Tsonopoulos, 1974, 1979).

The BMW/SV+x^3 EOS consumes up to one order of magnitude more CPU time than the BMW with second-virial correction EOS. We can see the influence of nested mole-fraction summations on the overall CPU time. The only difference between these two equations is that the former uses a cubic mixing rule for attractive-force parameter a

$$a = \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{k=1}^{m} x_i x_j x_k a_{ijk} \tag{10}$$

while the latter uses the classical quadratic mixing rule

$$a = \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j a_{ij} \tag{11}$$

This computing-time study shows that most of the CPU time is spent in calculating mixing-rule summations. The CPU time spent for the density-root iteration is minor; therefore, the complexity of the pure-fluid EOS (cubic or non-cubic) has only a relatively small effect upon total computational time.

HIGH-PRESSURE PHASE EQUILIBRIA

To illustrate the advantages of a non-cubic EOS with density-dependent mixing rules, we present high-pressure vapor-liquid equilibria (VLE) for two binary mixtures.

Figure 6 shows calculated and experimental (Heintz and Streett, 1982) VLE for the system hydrogen/ethane at 161.15 and 280.15 K. For this mixture of molecules differing significantly in size, The BMW/SV EOS correlates the phase behavior better than the CSW EOS.

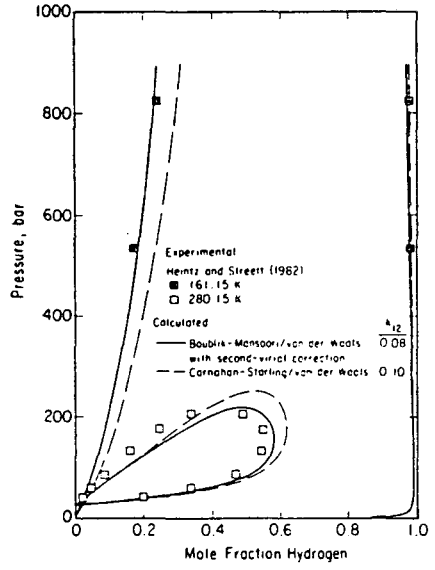

Fig. 6. Calculated and experimental vapor-liquid equilibria for hydrogen/ethane.

The CSW EOS uses classical mixing rules [eqn. (11)] with one binary interaction parameter k_{ij} to correct for small deviations from the geometric-mean combining rule for the attractive-force parameter

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \tag{12}$$

Pure-component parameters are fitted to vapor-pressure, liquid-density and supercritical-density data. Binary VLE data (K-factors) are used to fix binary interaction parameter k_{ij}. The numerical procedure is described elsewhere (Topliss, 1985). Table 1 gives values for the pure-component parameters. (Except for hydrogen, parameters $b^{(1)}$ and $b^{(2)}$ are set to zero.) Binary parameter k_{H_2/C_2H_6} is 0.1.

The BMW/SV EOS uses separate mixing rules for the low- and high-density regions. At high densities, the classical quadratic mixing rule [eqn. (11)] with binary interaction parameter k_{ij} [eqn. (12)] is used. At low densities, the EOS reduces to the

[5] Ely (1986) shows that the Boublik-Mansoori hard-sphere-mixture equation can be written as an EOS with density-dependent mixing rules reducing in the limit of low density to the Carnahan-Starling equation with van der Waals-1 mixing rules.

virial equation truncated after the second-virial-coefficient term. For the mixture, we use an empirical correlation for the mixture second virial cross coefficient (Tsonopoulos, 1974, 1979). For intermediate densities, a continuous function is used to interpolate between the two density limits (Prausntiz, 1985, and Cotterman and Prausnitz, 1986). Table 2 gives values for the pure-component parameters. Binary parameter k_{H_2/C_2H_6} is 0.08. Binary interaction parameter k^B for the second-virial-coefficient correlation (Tsonopoulos, 1979) is obtained independently from cross-second-virial-coefficient data; for this system it is 0.17.

TABLE 1

Pure-component parameters for the CSW EOS [eqns. (8) and (9)]

	$a^{(0)}$	$a^{(1)}$	$a^{(2)}$	$b^{(0)}$
Hydrogen	0.42955	0.26812	0.33333	[6]
Methane	0.49539	0.16199	0.33333	0.17841
Ethane	0.52738	0.12970	0.33333	0.17749
Water	0.50554	0.04939	0.33333	0.14279

[6] The temperature-dependence of van der Waals covolume parameter b for hydrogen is given by

$$b_{H_2} = \frac{RT_{c,H_2}}{P_{c,H_2}} \frac{0.20433 + 0.04533\,T^*_{H_2}}{1 + 0.33333\,T^*_{H_2}}$$

The BMW/SV EOS represents better than the CSW EOS the observed phase behavior for the low-density (high-temperature) vapor phase as well as for the high-density (low-temperature) liquid phase. This improvement follows from the flexibility of the density-dependent mixing rules to adjust independently the EOS parameters at low and high densities.

For most binary mixtures, eqn. (11) is sufficient to represent phase behavior using a single adjustable parameter k_{ij} [eqn. (12)]. However, for some highly asymmetric mixtures, it is advantageous to introduce a second adjustable parameter into the high-density mixing rule by using a cubic mixing rule for attractive-force parameter a [eqn. (10)]. The combining rule for a binary mixture is

$$a_{iij} = \frac{1}{3}a_i + \frac{2}{3}(a_i a_j)^{1/2}(1-k_{j,i}) \qquad (13)$$

for any permutation of indices iij. A similar equation holds for a_{ijj} and the second binary adjustable parameter $k_{i,j}$. The two binary parameters $k_{j,i}$ and $k_{i,j}$ adjust the attractive-force parameter a in separate concentration regions. When component i is infinetely dilute in component j, only parameter $k_{i,j}$ applies; at the opposite limit, when component j is infinetely dilute in component i, only parameter $k_{j,i}$ applies. At intermediate concentrations, both parameters are required. When $k_{i,j}=k_{j,i}$ the cubic mixing rule for attractive-force parameter a [eqn. (10)] reduces to the classical quadratic mixing rule [eqn. 11)].

TABLE 2

Pure-component parameters for the BMW/SV EOS [eqns. (8) and (9)]

	$a^{(0)}$	$a^{(1)}$	$a^{(2)}$	$b^{(0)}$
Hydrogen	0.42884	0.27149	0.33333	[7]
Methane	0.49191	0.16562	0.33333	0.17737
Ethane	0.52713	0.13233	0.33333	0.17750
Water	0.50482	0.05838	0.33333	0.14320

[7] The temperature dependence of van der Waals covolume parameter b for hydrogen is given by

$$b_{H_2} = \frac{RT_{c,H_2}}{P_{c,H_2}} \frac{0.20446 + 0.04590\,T^*_{H_2}}{1 + 0.33333\,T^*_{H_2}}$$

Figure 7 shows calculated and experimental (Sultanov et al., 1971, 1972, Olds et al., 1942, and Culberson and McKetta, 1951) VLE for the highly asymmetric binary mixture of methane/water at 310.95 and 510.95 K. The BMW/SV+x^3 EOS correlates the phase behavior significantly better than the CSW EOS. Tables 1 and 2 give pure-component parameters.

The BMW/SV+x^3 EOS uses two adjustable binary parameters to represent both water-rich and methane-rich concentration regions. To obtain good representation, the binary parameter for the water-rich end is temperature dependent, i.e. $k_{CH_4,H_2O}=0.28-189/T$ (T in K). The binary parameter k_{H_2O,CH_4} for the methane-rich phase is 0.38. Binary interaction parameter k^B for the second-virial-coefficient correlation (Tsonopoulos, 1979) is obtained independently from second-virial-cross-coefficient data; it is 0.29.

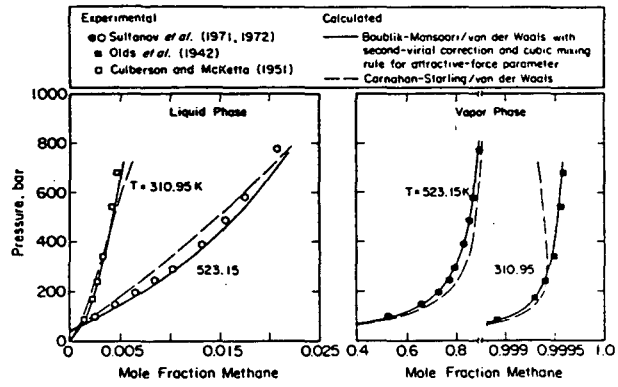

Fig. 7. Calculated and experimental vapor-liquid equilibria for methane/water.

For a fair comparison, we use the same number of binary adjustable parameters for the CSW EOS. Binary interaction parameter k_{ij} [eqn. (12)] is allowed to depend on temperature. Further, with much reluctance, we introduce a second binary interaction parameter l_{ij} into the mixing rule for van der Waals covolume parameter b [eqn. (7)]

$$b = \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j \left[\frac{b_i^{1/3}+b_j^{1/3}}{2}\right]^3 (1-l_{ij}) \qquad (14)$$

From VLE-data regression we obtain $k_{CH_4/H_2O}=0.94-106/T$ and $l_{CH_4/H_2O}=0.46$; the latter is physically absurd.

The density-dependent mixing rule provides flexibility independently to adjust the attractive-force parameter at the two dilute ends of the concentration region. This flexibility produces superior representation of phase behavior. While the classical mixing rules give a fairly good representation, they do so with binary interaction parameters that are physically unreasonable.

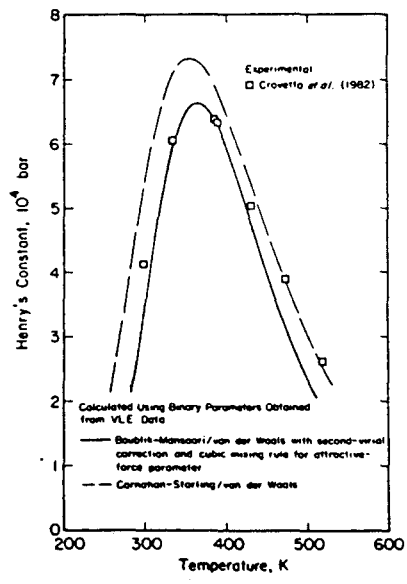

Fig. 8. Calculated and experimental Henry's constants for methane in water.

A stringent test for an EOS lies in its ability to represent limiting phase behavior correctly. Towards that end, we present in Figure 8 calculated and experimental (Crovetto et al., 1982) Henry's constants for methane in water as a function of temperature. We use the binary parameters obtained from VLE

data, given above.

Both EOS capture the essential features of the Henry's constant-versus-temperature plot. The use of temperature-dependent binary parameters is essential for achieving such good representation (Hu et al., 1984). The BMW/SV+x^3 EOS represents better the region near the maximum while the CSW EOS is better in the high-temperature region.

For the programs described here, computer software is available upon request to John M. Prausnitz.

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NOMENCLATURE

a	attractive-force parameter
b	van der Waals covolume parameter
k	binary interaction parameter
l	binary interaction parameter
m	number of components
N	total number of moles
n	number of moles
P	pressure
R	universal gas constant
T	temperature
x	mole fraction
$\underline{x}$	mole fractions

Greek letters

α	phase α
β	phase β
ρ	molar density
ϕ	fugacity coefficient

Subscripts

c	critical
des	desired
ext	extremum
i	component i
ij	interaction between components i and j
ijk	interaction between components i, j and k
i,j	interaction of component i (solute) with component j (solvent) when i is at infinite dilution
inf	inflection
lb	lower bound
lim	limiting
r	reduced
ub	upper bound

Superscripts

B	second virial coefficient
s	specified
(0)	0th coefficient etc. [see eqns. (8) and (9)]

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