Calculations of Complex Phase Equilibrium by Equal-Area Method

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The equal-area (EA) method is studied with respect to its applicability to a wide range of phase equilibrium scenarios for pure fluids and binary mixtures. The study covers vapor-liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), solid-liquid equilibrium (SLE) and their crossover transitions. The thermodynamic models studied include equation of state, activity coefficient and solid solubility models and their combinations. The performance of the EA method for chain molecules, at very low temperature and nearby the critical point is also investigated. We conclude that the EA method is very reliable and efficient and has a number of advantages over the conventional method. Finally, we apply the EA method to the regression of the model parameters to demonstrate its attractive application. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 591–599, 2012
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Introduction

Modeling of the physical and transport properties of materials and their behavior in mixtures—thermodynamic (or phase) equilibrium, chemical equilibrium, chemical reaction, mass transfer—is the foundation of process flowsheet simulation. Phase equilibrium calculations, often referred to as flash calculations, are associated with most unit operation models of a flowsheet, e.g., distillation columns, pressure vessels, tanks, heat exchangers, and valves. A robust and reliable algorithm for calculating phase equilibria is essential to the success of process simulation. The algorithm must correctly identify the phases, must find the true solution, must be numerically stable, and must be as computationally efficient as possible. Traditionally, computational efficiency has not been of particular concern. However, with the increasing prevalence of dynamic simulation and increasing deployment of flowsheet models in applications critical to the operation of industrial plants, such as optimizing control, the computational efficiency of flash calculations has become much more important. Intuitively, a good algorithm should be grounded in the physical world and have a sound mathematical basis.

The conventional method to phase equilibrium calculations equates the pressures and chemical potentials of the phases. In fact, pressure and chemical potential are derivatives of the Helmholtz free energy for pure fluids or the Gibbs free energy for mixtures. More fundamentally, phase equilibrium is the state at which the free energy is minimized. However, although equality of the pressure and chemical potential for the phases are necessary conditions for phase equilibrium, they are not sufficient conditions. Consequently, the conventional method can fail to identify the phases present in the mixture or can yield a solution that is nonphysical. For some extreme conditions, such as very low temperature, high pressure or low concentration, it is

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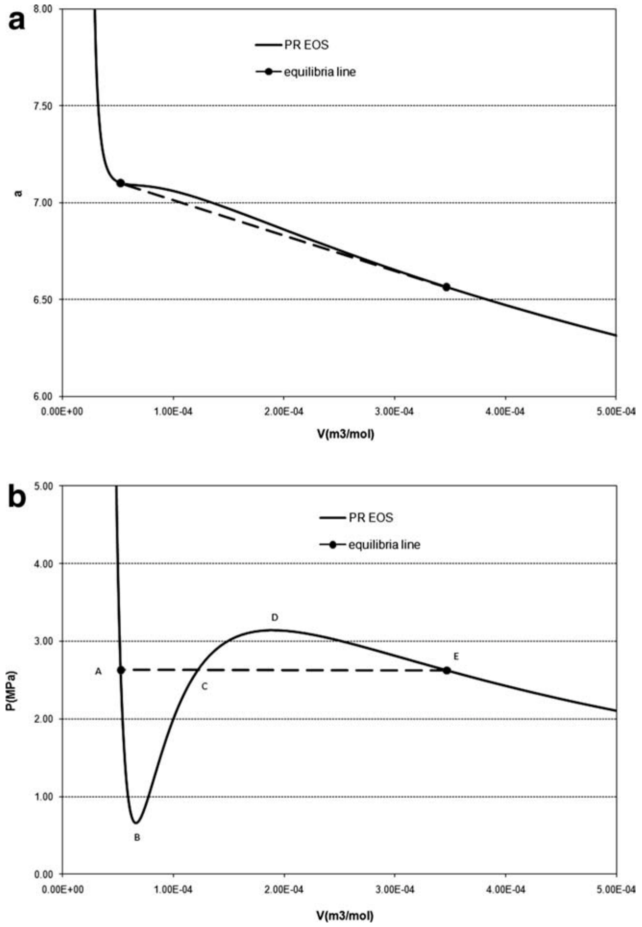

Figure 1. (a) Helmholtz free energy versus volume for CH_4 at 173.15 K. (b) Pressure versus volume for CH_4 at 173.15 K.

Points A and E correspond to liquid and vapor volumes at saturation.

possible for equilibrium to shift between VLE, LLE, and VLLE as a result of small changes in the conditions of the flash. Another important case is calculation of phase equilibrium nearby the critical point, where both first and second derivatives of free energy tend to go to zero. At these conditions, the conventional method can be unstable[1] and/or require a large number of iterations to achieve convergence. Consequently, the computation time, which is a significant impediment for process simulation, especially for dynamic simulation, will increase. For noncubic equation of state models, such as statistical associating fluid theory (SAFT), closed form expressions for the pressures and chemical potentials of the phases cannot be formulated. This requires that an additional step be added to the conventional method to first calculate the density. Therefore, a better method for calculating phase equilibria is always being sought. This method is expected to be physically rational, independent of the thermodynamic model and insensitive to the conditions at which equilibrium is calculated (temperature, pressure, etc). It is intuitive that a method developed fundamentally from the free energy instead of its conventional derivatives will be the most promising.

The Equal Area method[2–6] is an algorithm for calculating phase equilibrium that is particularly well suited for pure fluids and binary mixtures. As illustrated in Figure 1a for a pure fluid, it determines phase equilibrium by constructing a line that is tangent to the nonconvex curve of the Helmholtz free energy for pure fluids or of Gibbs free energy for (binary) mixtures at two points. Connecting the corresponding points on the curve of the derivative of the free energy by a (horizontal) line [Figure 1(b) for a pure fluid, Figure 2 for a binary mixture] creates two segments having equal areas. When phase equilibrium exists, these segments of equal area must exist. The line defines two equilibrium points as shown in Figures 1(b) and 2. If the free energy curve is convex over the whole volume or concentration range, only a single phase exists and no further calculations are required. Therefore, the equal-area (EA) method gives a clear picture of whether phase equilibrium exists and how we determine its values.

To the best of our knowledge, application of the EA method has been reported only for limited cases, specifically, its application to cubic equation of state models[2,4–6] and activity coefficient models[3,6] for small molecules. In both cases, the computation was carried out at moderate conditions. This article explores the application of the EA method to a much wider range of cases. Considering potential industrial applications, we address the following topics of particular relevance for process simulation:

(1) Multiple types of phase equilibrium scenarios

(2) Noncubic equation of state models

(3) Two-fluid VLE models, in which the vapor phase is represented by an EOS model and the liquid phase is represented by an ACM

(4) SLE model in which the liquid phase is represented by an EOS model and solid-liquid equilibrium is represented by a solubility model

(5) Polymer solutions

A comparison with the conventional method is also presented. We conclude with a demonstration of the application

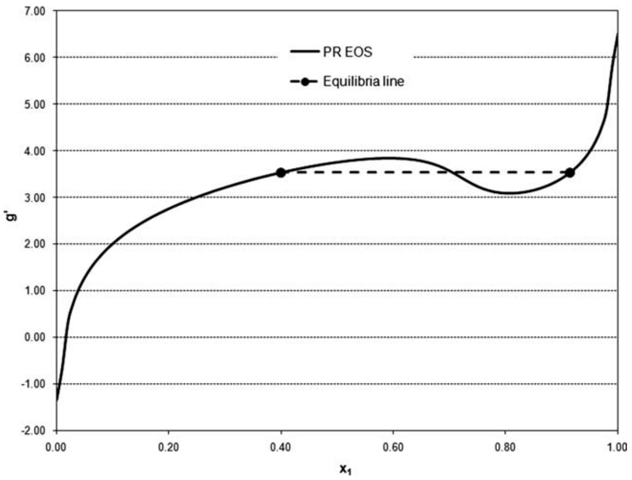

Figure 2. Derivative of Gibbs free energy versus composition for $CH_4(1)$ + $n\text{-}C_4H_{10}(2)$ at 294.15 K and 75 bar calculated by the PR equation of state.

Two points correspond to concentrations at equilibrium.

of the EA method to the regression of the parameters of a SAFT model.

Before proceeding, we note that the details (formulas and parameters) of the thermodynamic models can be found in relevant papers or textbooks. They are not repeated here, since we are focusing on the computational characteristics of thermodynamic equilibrium calculations.

Summary of the Equal Area Method

For a detailed presentation of the EA method, see Hanif et al.[4] for pure fluids and Eubank and Hall[3] for mixtures. We present here only a brief review of the relevant equations.

Pure fluid. The physical behavior of a pure fluid is determined by the basic relations

$$G = A + PV \tag{1}$$

$$P = -\left.\frac{\partial A}{\partial V}\right|_T \tag{2}$$

where G, A, P, T, and V are Gibbs free energy, Helmholtz free energy, pressure, temperature and volume, respectively. For the saturated vapor and liquid states, $G^v = G^l$ and $P^v = P^l$. The two relations give

$$\left(\left.\frac{\partial A}{\partial V}\right|_T\right)^v = \left(\left.\frac{\partial A}{\partial V}\right|_T\right)^l = \frac{A^l - A^v}{V^l - V^v} \tag{3}$$

Then, integrating $\partial A/\partial V|_T$ from V^v to V^l yields the equal area relationship

$$\left(\left.\frac{\partial A}{\partial V}\right|_T\right)^v = \left(\left.\frac{\partial A}{\partial V}\right|_T\right)^l = \frac{1}{V^l - V^v}\int_{V^v}^{V^l}\left(\left.\frac{\partial A}{\partial V}\right|_T\right)dV \tag{4}$$

Or in implementing the EA method

$$P^s = -\frac{\int_{V^v}^{V^l}\left(\left.\frac{\partial A}{\partial V}\right|_T\right)dV}{V^l - V^v} \tag{5}$$

where the subscripts l, v, and s stand for the liquid, vapor and saturation states, respectively. The Eqs. 3–5 are identical to those of Eubank and Hall,[3] The tangent line of the Helmholtz free energy for pure methane is shown in Figure 1(a). The corresponding curve of pressure, P^s, is shown in Figure 1(b). Referring to Figure 1(b), it follows that joining V^l (point A) and V^v (point E) by a straight (horizontal) line creates two curve segments, one below P^s (curve segment ABC) and one above (curve segment CDE), whose areas are equal. This equality is fundamental to implement the EA method.

Binary mixture. For a binary mixture at fixed temperature and pressure, the Gibbs free energy is commonly expressed as

$$G = (N_1 + N_2)g\left(\frac{N_1}{N_1 + N_2}\right) = (N_1 + N_2)g(x_1) \tag{6}$$

wherein g is reduced Gibbs free energy, x is composition, and subscripts 1 and 2 represent compounds 1 and 2, respectively. From Eq. 6, the chemical potential, μ, can be expressed for each compound as

$$\mu_1 = \frac{\partial G}{\partial N_1} = g(x_1) + (1 - x_1)\left.\frac{\partial g(x_1)}{\partial x_1}\right|_{T,P} \tag{7}$$

and

$$\mu_2 = \frac{\partial G}{\partial N_2} = g(x_1) - x_1\left.\frac{\partial g(x_1)}{\partial x_1}\right|_{T,P} \tag{8}$$

Subtracting Eq. 8 from Eq. 7 yields

$$\left.\frac{\partial g(x_1)}{\partial x_1}\right|_{T,P} = \mu_1 - \mu_2 \tag{9}$$

Equation 9 is a general relation of thermodynamics and is independent of phase state. When phases α and β are in thermodynamic equilibrium, their chemical potentials must be equal so that

$$\left.\left(\frac{\partial g}{\partial x_1}\right)^\alpha\right|_{T,P} = \left.\left(\frac{\partial g}{\partial x_1}\right)^\beta\right|_{T,P} = \frac{g^\alpha - g^\beta}{x_1^\alpha - x_1^\beta} \tag{10}$$

Integrating $\partial g/\partial x_1|_{T,P}$ from x_1^α to x_1^β yields

$$\int_{x_1^\beta}^{x_1^\alpha}\left.\left(\frac{\partial g}{\partial x_1}\right)\right|_{T,P} dx_1 = g^\alpha - g^\beta \tag{11}$$

and then substituting into Eq. 10 yields the equal area relationship for binary mixtures

$$\left.\left(\frac{\partial g}{\partial x_1}\right)^\alpha\right|_{T,P} = \left.\left(\frac{\partial g}{\partial x_1}\right)^\beta\right|_{T,P} = \frac{1}{x_1^\alpha - x_1^\beta}\int_{x_1^\beta}^{x_1^\alpha}\left.\left(\frac{\partial g}{\partial x_1}\right)\right|_{T,P} dx_1 \tag{12}$$

which is mathematically equivalent to Eq. 4 after replacing -A with g and V with x_1. It is worthwhile to mention here that g is a function of T, P, and x_1, and is independent of x_2. This equal area relation for a binary mixture of methane and *n*-butane is shown in Figure 2.

For a pure fluid, Eq. 4 implies two relations to be solved for V^α and V^β. Correspondingly, Eq. 12 implies two relations to be solved for x_1^α and x_1^β for binary mixtures. From the principle of free energy minimization, when phases split, a unique solution must exist.

Implementation of the EA Method

When implementing the EA method, a number of practical matters had to be addressed. For a pure fluid, $P \rightarrow 0$ as $V \rightarrow \infty$, which can be numerically very troublesome. When temperature drops from 173.15K in Figure (1b) to 100K in Figure 3(a), the EA area shrinks severely and it shrinks even more with increasing temperature drop. This difficulty was avoided by using density instead of volume, as shown in Figure 3(b). Replacing V by density, ρ, in Eq. 5, we obtain

$$P^v = P^l = \frac{RT\rho^l\rho^v}{\rho^l - \rho^v}\left(a^l - a^v\right) \tag{13}$$

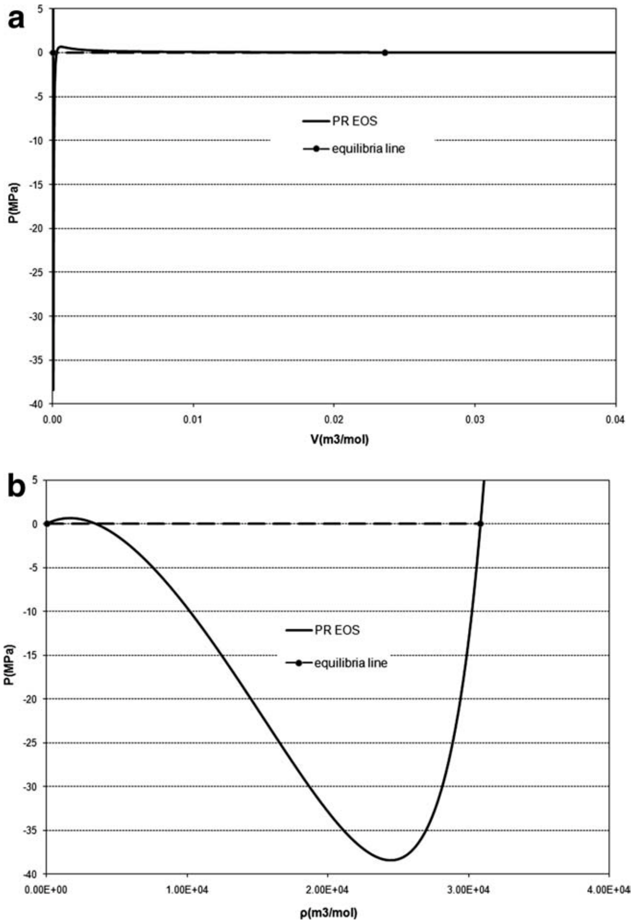

Figure 3. (a) Pressure versus volume for CH_4 at 100K. (b) Pressure versus density for CH_4 at 100K.

wherein $\alpha = A/NRT$ is the reduced Helmholtz free energy and is uniquely specified in a given thermodynamic model. Procedurally, the EA calculation for pure fluids is performed as follows:

(1) Find two spinodal points for P, that is, two points for which $\partial P/\partial \boldsymbol{\rho} = 0$. For a pure fluid, the existence of two such points indicates the presence of two saturated phases, liquid and vapor or liquid and solid. Just a single phase is present when $\partial P/\partial \boldsymbol{\rho} > 0$ throughout the whole density range. The two spinodal points can be determined by a numerical method such as the interval-Newton method presented by Hua et al.[7]

(2) Determine the nature of the phase (vapor-like or liquid-like) for each spinodal point. The spinodal points must appear in pairs. If this is not the case, the associated thermodynamic model is physically irrational and should not be used. Referring to Figure 1(b), for a pure fluid the lower (A) and higher (E) spinodal points correspond to the liquid-like and vapor-like densities, respectively.

(3) Use the two spinodal points, that is, the liquid-like and vapor-like phase densities, as initial values to begin the iterative calculation of the pressure using

$$P_{n+1} = \frac{RT\rho_n^l\rho_n^v}{\rho_n^l - \rho_n^v}\left(a_n^l - a_n^v\right) \tag{14}$$

(4) Iterate until P is stationary within a given tolerance. At convergence, P is the saturation pressure and the two associated densities are the saturated vapor and liquid densities, respectively. This calculation is very efficient and it often takes only a few iterations, as also mentioned by Eubank and Hall.[3]

Table 1 shows the details for this iterative process using pure propane as an example. In the first iteration, the pressure is calculated from the average of two spinodal pressures. The average pressure is negative and thus gives negative vapor density. To allow the iterative process to proceed, the negative density is simply set by a floor value 10^{-14}. In this example, it takes only seven iterations to achieve our goal. For binary mixtures, the calculation procedure is analogous to that for pure fluids. In this instance, $\partial g(x_1)/\partial x_1|_{T,P} = 0$ defines two "spinodal" points. The analogy can be seen by comparing Figure 1(b) with Figure 2.

Applications of the EA Method

Pure Fluids. Figure 1(b) shows the phase equilibrium calculated by the EA method for methane at 173.15 K using the Peng-Robinson (PR) equation of state. Figure 4 shows the same phase equilibrium scenario but using the Perturbed-Chain SAFT (PC-SAFT) model.[8] Even though the EOS models are quite different and thus give different pressure-volume curves, the principle of two equal areas holds in both cases. We found that the determination of the phase status inherent in the EA method is critical to identifying the correct phase behaviors. During the numerical process, $(\partial P/\partial\rho)_T$ is calculated. When $(\partial P/\partial\rho)_T$ is greater zero over the whole range of density, the fluid is single phase and the algorithm terminates, avoiding unnecessary calculations.

The conventional calculation of phase equilibrium solves the two equations

$$P^l = P^v, \quad \mu^l = \mu^v \tag{15}$$

for ρ^v and ρ^l. Experience shows that the solution can by very sensitive to temperature, pressure and initial conditions. For

Table 1. EA Iteration to Calculate the Saturated Densities (mol/m^3) and Vapor Pressure (Pa) of Propane at $T = 60$K Using PR EOS

Iter=	1	2	3	4	5	6	7
P_{old}	−8.4E+07	2.40E-11	7.94E-11	1.61E-10	2.04E-10	2.07E-10	2.07E-10
P_{left}	1.00E-14	5.15E-14	1.70E-13	3.45E-13	4.38E-13	4.44E-13	4.44E-13
P_{right}	16955.61	17211.24	17211.24	17211.24	17211.24	17211.24	17211.24
P_{new}	2.40E-11	7.94E-11	1.61E-10	2.04E-10	2.07E-10	2.07E-10	2.07E-10

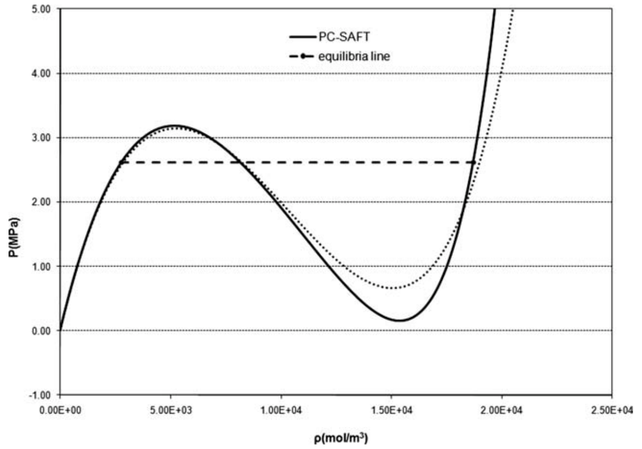

Figure 4. Pressure versus volume for CH_4 at 173.15 K by PC-SAFT.

The solid curve is given by PC-SAFT and the dashed one by PR equation of state for comparison.

non-CEOS models, the solution becomes more complicated because the fluid density must be calculated numerically rather than analytically. We compare the EA method with the conventional method using a Newton–Raphson iterative solution of Eq. 15 in Figure 5(a). The saturated pressure of *n*-hexadecane ($T_c = 723$ K) is calculated by both methods. The calculation is performed for very low temperatures and hence is very sensitive to numerical stability. Figure 5(a) clearly shows that the EA method performs very well for temperatures as low as 190 K and pressures as small as 1.0E-12 kPa. On the other hand, the conventional method using Newton-Raphson, fails for temperatures below ~250 K. In addition, to achieve reliable convergence of the Newton-Raphson iterative solution, good initial values ($\rho^v = 0$, $\rho^l = 3000$), very close to true solution, were required.

Binary Mixtures Nearby the Critical Point. It is well known that phase equilibrium calculations can be extremely difficult for some physical conditions such as low temperatures, high pressures, nearly pure mixtures and for conditions nearby the critical point. Here we look more closely at the calculation of phase equilibrium for conditions nearby the critical point, where special treatments are typically introduced to achieve reliable solution. For example, Stapley and Luks[9] use complex roots of the cubic equation of state in their treatment. In our evaluation of the EA method, we choose the mixture $CH_4(1)$ + n-$C_4H_{10}(2)$ at 294.15 K for solving the phase equilibrium. In the solution, both the EA method and Newton iterative method are employed with incrementally increasing pressure toward the critical value. As shown in Figure 5(b), the EA method continues to yield a solution as the critical pressure is approached. At its achieved maxium pressure—137.087 bar, the mole fractions of CH_4 in the liquid and vapor phases are determined to be 0.783 and 0.784, respectively. From these results we extrapolate the critical pressure and critical mole fraction of CH_4 to be 137.088 bar and 0.7835. In contrast, the conventional method, employing Newton iterative solution, fails to solve above pressures of ~136.84 bar and goes astray physically above pressures of ~135.5 bar.

Binary Mixtures Represented by Two-Fluid Models. The application of the EA method to binary mixtures in which the mixture is represented by a single thermodynamic model, CEOS model or ACM, the so-called one-fluid model, has been reported previously.[2–6] In this work, we focus on two-fluid models, in which the vapor phase is represented by an EOS model and liquid phase is represented by an ACM. Two-fluid models are commonly used in process simulation due to their better prediction accuracy achieved by representing the vapor and liquid phases individually.

For one trial, we examined the VLE calculations for the mixture Methanol(1) - 1.2-Dichloroethane(2) at 323.15 K and 0.6211 bar presented by Reid et al.[10] The vapor phase is modeled as an ideal gas and the liquid phase is represented by the Van Laar activity coefficient model. Figure 6 shows the full curve of $\partial g(x_1)/\partial x_1|_{T,P}$ versus x_1, the mole fraction of methanol, for the EA calculation. The figure shows the existence of two equilibriums: one with $x_1 = 0.1785$ and $y_1 =$

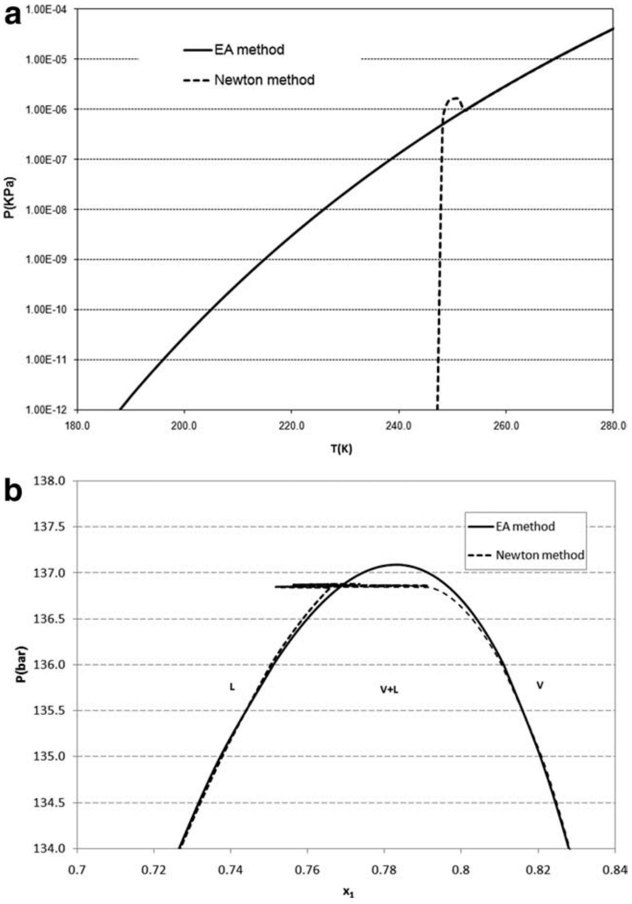

Figure 5. (a) A comparison between the EA method and the conventional method, employing a Newton iterative solution, to calculate the saturated pressure for *n*-hexadecane by the PR equation of state; (b) critical region calculation of mixture $CH_4(1)$ + n-$C_4H_{10}(2)$ with 294K using the EA method and the conventional method, employing a Newton iterative solution.

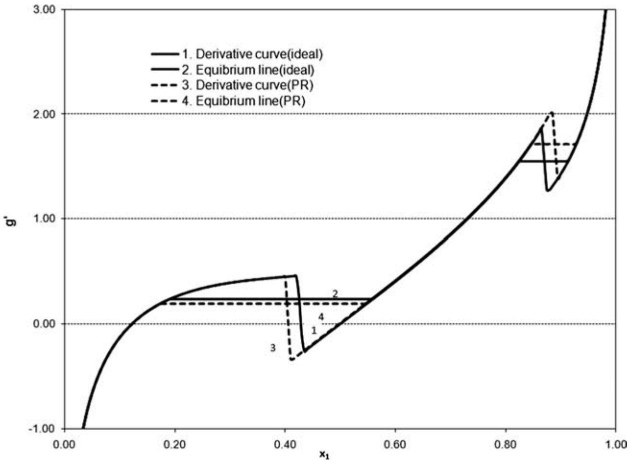

Figure 6. Phase equilibrium for Methanol + 1,2-dichloroethane at 323.15 K and 0.6211 bar, using ideal and Vanlaar models and PR and Vanlaar models, respectively.

0.5430 and the other with $x_1 = 0.9284$ and $y_1 = 0.8463$. The first equilibrium coincides with the result in Reid et al. The unreported second equilibrium is shown here to illustrate the special capability of EA method. We also found that when the vapor phase is modeled using the PR equation of state, similar predictions are observed, although, of course, the equilibrium values are somewhat different. To probe these predictions more deeply, we plotted the Gibbs free energy of the mixture. Figure 7 shows that the curves of Gibbs free energy for the vapor and liquid phases cross at two points, $x_1 = \sim 0.43$ and $x_1 = \sim 0.87$. When x_1 is less than ~0.43 or greater than ~0.87 the Gibbs free energy of the liquid phase is lower, while between these values the Gibbs free energy of the vapor phase is lower. Consequently, there are two qualifying tangents to the curve of minimum Gibbs free energy so two equilibriums exist as shown in Figure 6. It can be deduced that when the temperature is increased, the free energy of the gas phase will eventually fall below that of the liquid phase at which point the second equilibrium (VLE2 in Figure 7) will disappear. As the temperature is increased further, both equilibriums will eventually disappear. Similarly, when the temperature is decreased, the free energy of the liquid phase will fall below that of the gas phase and the equilibriums will eventually disappear. Complex cases such as this can be very challenging for the conventional method.

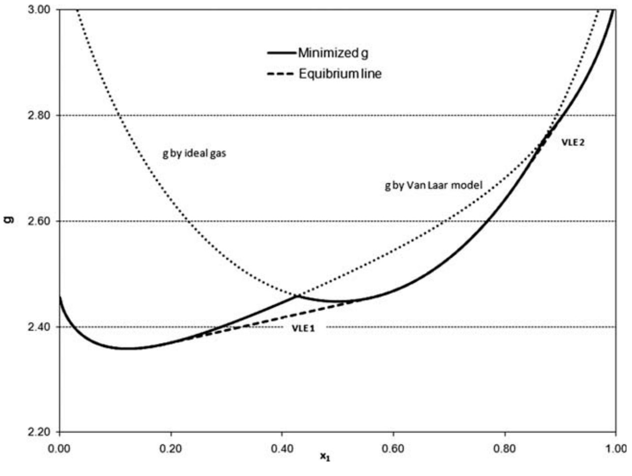

Figure 7. Intersection between free energy of ideal vapor phase and of liquid phase with Vanlaar model.

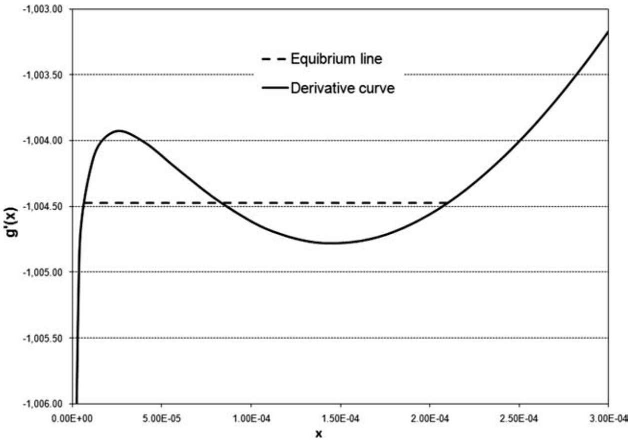

Figure 8. Derivative of Gibbs free energy versus composition for PP + *n*-Pentane at 470.15 K and 70 bar by PC-SAFT.

Problems with the conventional method have been reported by Nishawn et al.[5] In calculating the phase diagram for the mixture of *n*-butane and water using the PR equation of state model, they found that with increasing pressure, the conventional method incorrectly predicts VLE instead of physically correct LLE. This error is not encountered with the EA method. In another case for Lennard-Jones (LJ) model mixtures, using the EA method, Tang and Lu[11] found that there should be a phase transition between LLE, VLLE, and VLE with increasing temperature. Using the conventional method can lead to the erroneous conclusion that LLE exists up to the upper critical solution temperature, missing the transition to VLLE which, in fact, occurs at a temperature below the USCT.

Polymers. Using statistical thermodynamics, polymers or chain molecules are decomposed into segments, that is, substructures of molecules of which the polymer or chain molecule is composed. A polymer or chain molecule is described by its number of segments, the statistical distribution of the segments and their size and attractive interaction. In general, a polymer molecule consists of thousands of segments. The molar concentration for a segment (e.g., ~1.0E-5) can be several orders of magnitude smaller than its corresponding mass concentration (e.g., ~0.1). This presents a challenge for traditional calculation methods for phase equilibrium.[12] For one trial, we chose the mixture of polypropylene (PP) and *n*-pentane, which Gross and Sadowski[13] modeled using the PC-SAFT EOS model with the mono-dispersive assumption for PP, in which PP is represented by a single molecular substructure. Using the EA method and paying particular attention to the sensitivities noted above, we obtained LLE

Table 2. Parameters of Water for PC-SAFT and FMSA-SAFT Regressed from Temperature 388 to 582 K (0.6–0.9Tc)

						AAD	
	σ	ε	m	κ^{AB}	ε^{AB}	ρ^L	P^{sat}
PC-SAFT	3.0007	366.51	1.06	2500.7	0.03487	0.047	0.022
FMSA-SAFT	3.0863	463.48	0.9933	2585.9	0.0354	0.020	0.013

with x_{L1} = 5.83E-6 and x_{L2} = 2.15E-4, as shown in Figure 8, where x_{L1} and x_{L2} are the mole fraction of the polymer in the two liquid phases. These values coincide with the results reported by Gross and Sadowski.

In general, polymers present in solvents as poly-dispersive, that is, a chain molecule composed of multiple segments having different molecular substructures. In principle, polymers should be treated as multicomponent mixtures, which calculation can be complicated by the EA method when the number of components is very large. However, recent work by Jog and Chapman[14] shows that poly-dispersity can be represented by a single pseudo-component when the segment distribution follows specific patterns. This work shows promise for extending application of the EA method, with its known advantages, to more general cases.

Complex Phase Equilibrium. By complex phase equilibrium we mean equilibrium scenarios in which three or more phases can coexist. To illustrate the capability of the EA method for complex phase equilibrium calculations, we selected the binary mixture of water and phenol recently reported by Tumakakaa et al.[15] as a test case. This binary mixture is used in particular crystallization processes; for these crystallization processes, LLE and VLE is of particular concern during purification. Tumakakaa et al. concluded that PC-SAFT is the best choice of thermodynamic model for this case and demonstrated that with decreasing temperature the mixture transitions through the following phases: single phase vapor, VLE, single phase liquid, LLE, SLE, and finally single phase solid. These are all the phases expected in process simulation for industrial applications. In this study, these equilibrium transitions were predicted using the EA method, like Tumakakaa et al., with the PC-SAFT thermodynamic model to represent both the vapor and liquid phases and the solid solubility model suggested by Reid et al.[10] to represent solid-liquid equilibrium. The parameters of the PC-SAFT model can be found in the first row of Tables 1 and 2. Figures 9 and 10 clearly show that the EA method correctly predicts all the phases and transitions. Of particular note, Figure 10 shows that for temperatures between 278 and 313.57 K three equilibriums are possible—SLE, single phase liquid, and LLE. Using the EA method, all three equilibriums were found in a manner similar to that used when constructing Figures 6 and 7. The conventional method can be very problematic for transitions from SLE and LLE to single phase solid since its solution mathematically remains feasible but is physically impossible. The EA method avoids this pitfall due to its inherent physical stability analysis.

Parameter Regression. Parameter regression is indispensable for ensuring that thermodynamic models reflect the behavior of real fluids. For instance, a general SAFT model has three parameters for each component (segment size, σ, energy strength, ε, chain length, m) and one binary interaction parameter k_{12} for each pair of nonassociating components. For associating components, at least two additional parameters (cross-interaction strength, κ^{AB}, and volume, ε^{AB}) are required for each pair of components. These parameters are regressed using pure fluid property data and equilibrium mixture data. For mixtures, all commonly used models need only binary interaction parameters, which can be regressed from VLE or LLE data of two-compound mixtures. As the EA method has many advantages as we have discussed for both pure components and binary mixtures, it is well suited

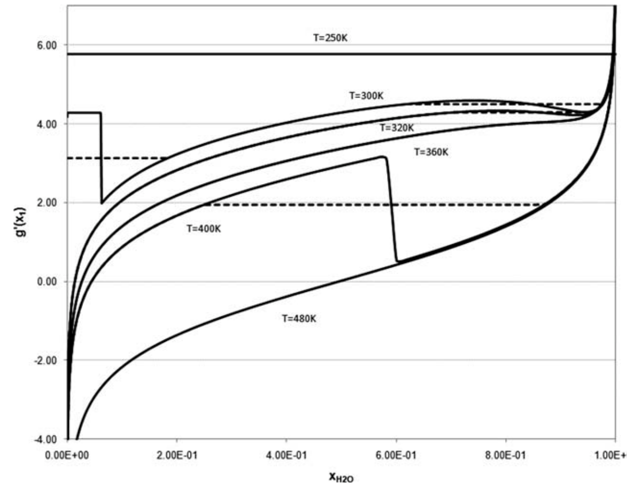

Figure 9. Derivative of Gibbs free energy versus composition for water + phenol at 1 atm for PC-SAFT.

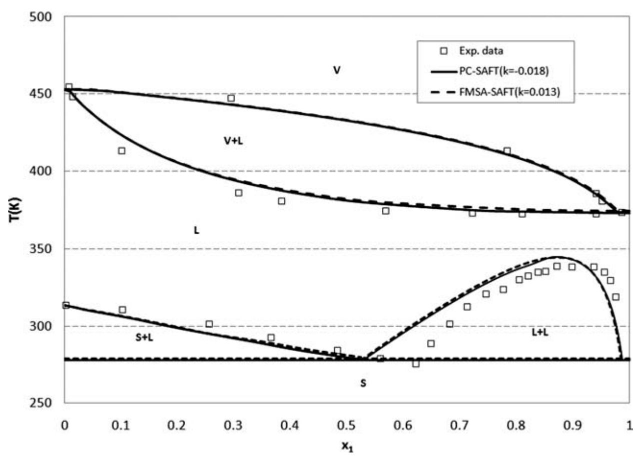

Figure 10. VLE+LLE+SLE of water + phenol calculated by PC-SAFT and FMSA-SAFT at 1 atm.

Table 3. Parameters of Phenol for PC-SAFT and FMSA-SAFT Regressed from Temperature 416 to 624 K (0.6–0.9Tc)

						AAD	
	σ	ε	m	κ^{AB}	ε^{AB}	ρ^L	P^{sat}
PC-SAFT	3.5660	250.37	2.6844	2827.6	0.0866	0.0088	0.089
FMSA-SAFT	3.7064	328.67	2.5636	2403.2	0.0844	0.0022	0.01

to parameter regression. In our work, we applied the EA method to regress the parameters of first-order mean spherical approximation SAFT model (FMSA-SAFT)[11,16] to data for the same mixture of water and phenol discussed above. We chose the FMSA-SAFT model because it is more theoretically rigorous and applies to both homogeneous and inhomogeneous fluids.[16,17] For the mixture of water and phenol, the FMSA-SAFT model has the same number of parameters as the PC-SAFT model. Pure component data for regression were generated using the DIPPR database. The second row of Tables 2 and 3 show the regressed values for the parameters as well as the absolute average deviations (AAD) of the predictions from those generated by DIPPR. The binary interaction parameter ($k_{12} = 0.013$) was fitted using experimental LLE data extracted from Tumakakaa et al.[15] as shown in Figure 10. With these parameters, we calculated the complete phase diagram in this figure. Comparing the AAD values for the PC-SAFT and FMSA-SAFT models in Tables 2 and 3 and comparing the equilibrium curves in Figure 10, shows that FMSA-SAFT is slightly better in AADs due to parameter regression but there is little difference between the two models in Figure 10 for this highly associating mixture.

Comments and Conclusions

In this work we have shown that the EA method applies to a wide range of equilibriums and thermodynamic models. We investigated through several examples the calculation of VLE, LLE, VLLE and SLE and their transitions. The thermodynamic models in our investigations included cubic equations of state, noncubic equations of state, activity coefficient, and solid-liquid saturation models and their combinations. We conclude that the EA method yields rational results, that is, it finds all the physical equilibriums and does not produce nonphysical equilibriums for pure fluids and binary mixtures. The algorithm is robust, even for extreme conditions of very low temperature, very low pressure, nearly pure mixtures, and for conditions nearby the critical point.

Finally, we demonstrated that the EA method is particularly well suited to parameter regression of thermodynamic models, using the FMSA-SAFT model as an example.

For comparison, we have shown that a straightforward Newton iterative solution of the conventional method can yield misleading results so it needs extra attention in its implementation. We also made some comparisons with Michelsen's method[18] for our cases. The method, available as the GPEC[19] code, can be widely used to calculate phase envelops for both binary and other mixtures. Although it works very well for many types of mixtures, Michelsen's method remains to be validated for special equilibrium cases and more recently developed thermodynamic models, since it has some empirical aspects in its iterative solution approach. In testing with GPEC, we found that it crashed for phase equilibrium calculation of PP + *n*-Pentane shown in Figure 8. We note that the SAFT EOS is used in this example. Therefore, we cannot presume that a single method is suitable for all phase equilibria.

From a practical perspective, the EA method is computationally efficient for pure fluids and binary mixtures, although its extension to multicomponent mixtures has been reported.[4,20] Specially, it is capable of calculating, as we show here, the global phase physical behavior—vapor, liquid, solid and their coexistences and transitions. A less obvious advantage of the EA method is that its implementation requires only fundamental information—Helmholtz or Gibbs free energy. In the conventional method, other properties, such as pressure and chemical potential, which are derived from the free energy, are required, increasing the computational effort. Together with its capability for calculating equilibrium over a wide range of conditions, we feel that it is a powerful tool for thermodynamic computation, especially in simulation of industrial process.

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