Complex Multiphase Equilibrium Calculations by Direct Minimization of Gibbs Free Energy by Use of Simulated Annealing

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Summary
The computational problems in reservoir fluid systems are mostly in the critical region and in liquid-liquid (LL), vapor-liquid-liquid (VLL), and higher-phase equilibria. The conventional methods to perform phase-equilibrium calculations with the equality of chemical potentials cannot guarantee a correct solution.

In this study, we propose a new method to calculate the equilibrium state by direct minimization of the Gibbs free energy of the system at constant temperature and pressure. We use the simulated annealing (SA) algorithm to perform the global optimization. Estimates of key parameters of the SA algorithm are also made for phase-behavior calculations. Several examples, including (1) VLL equilibria in the critical region, (2) VLL equilibria for reservoir fluid systems, (3) VLL equilibria for an H2S-containing mixture, and (4) VL-multisolid equilibria for reservoir fluids, show the reliability of the method.

Introduction
Consider the multicomponent-multiphase flash at constant temperature and pressure sketched in Fig. 1. The equilibrium state consists of $n_p$ phases; each phase $j$ consists of $n_{j1}, n_{j2}, \ldots, n_{jn_j}$ moles. From the second law of thermodynamics, the equilibrium state is a state in which the Gibbs free energy of the system is a minimum. The minimum of Gibbs free energy is a sufficient and necessary condition for the equilibrium state. At constant temperature and pressure (note that all calculations will be performed at this condition), the Gibbs free energy of the system in Fig. 1 can be written as

\[ G = \sum_{j=1}^{n_p} G_j \left( n_{j1}, n_{j2}, \ldots, n_{jn_j} \right) \]  

(1)

where $G_j$ is the Gibbs free energy of Phase $j$, and $G$ is the total Gibbs free energy of the system. When $G$ is minimized with respect to $n_{ij} (i = 1, 2, \ldots, n_j; j = 1, 2, \ldots, n_p)$ subject to the following constraints:

1. material balance of Component $i$,

\[ n_i = \sum_{j=1}^{n_p} n_{ij} \]  

(2)

2. the non-negative mole number of Component $i$ in Phase $j$,

\[ 0 \leq n_{ij} \leq n_i (i = 1, 2, \ldots, n_i; j = 1, 2, \ldots, n_p) \]  

(3)

The optimized values, $n^*_{ij} (i = 1, 2, \ldots, n_i; j = 1, 2, \ldots, n_p)$, are the mole numbers of the equilibrium state; the global minimization with the constraints is difficult to implement; as a consequence, direct minimization of the Gibbs free energy has not been widely applied.

Conventional Approach for Phase-Equilibrium Calculations
The equality of chemical potentials of each species in all phases is often used to perform the phase-equilibrium calculations:

\[ \mu_{i1} = \mu_{i2} = \ldots = \mu_{in_j} \]  

(4)

The number of equations in Eq. 4 is $n_i \times (n_j - 1)$, plus $n_i$ material-balance equations given by Eq. 2; a total of $n_i \times n_j$ equations are provided. The mole numbers $n_{ij} (i = 1, 2, \ldots, n_i; j = 1, 2, \ldots, n_p)$ of the equilibrium state are determined by solving these $n_i \times n_j$ nonlinear equations. The widely used solution methods are the successive substitution method through phase-equilibrium constants $K_j (i = 1, 2, \ldots, n_i)$ and direct application of the Newton method. Both approaches require an initial guess and work quite well for VL equilibria except in the near-critical region. In the critical region, the successive substitution becomes intolerably slow and the Newton method may fail when the initial guess is not close to the true solution. In LL and VLL equilibria, both methods may compute false solutions. The falseness is because Eq. 4 is only a necessary condition for an equilibrium state. The tangent-plane-distance (TPD) approach has been introduced to recognize the false solution. The concept of stability analysis is used to derive the TPD.

Tangent-Plane-Distance Approach
Suppose $\bar{w}$ is a given overall composition. The mathematical expression of the TPD function is

\[ D(\bar{w}) = \sum_{i=1}^{n_i} \bar{u}_i [\mu(\bar{w}) - \mu_i(\bar{w})] \]  

(5a)

where $D(\bar{w})$ is the distance function between the Gibbs free energy surface and its tangent plane at composition $\bar{w}$. When $D(\bar{w})$ is minimized with respect to $u_i (i = 1, 2, \ldots, n_i)$ subject to

\[ \sum_{i=1}^{n_i} u_i = 1 \]  

(5b)

and $0 \leq u_i \leq 1 (i = 1, 2, \ldots, n_i)$,

\[ D^* \geq 0 \]  

(5c)

the optimized value, $D^*$, provides the stability analysis of the mixture at composition $\bar{w}$. If $D^* < 0$, the system is unstable. The optimized composition $\bar{w}^*$ is a good approximation of the incipient phase composition. The application of TPD criterion improves the reliability of conventional-phase-equilibrium by providing a guideline to judge that the mixture is absolutely stable. When unstable, a good initial composition $\bar{w}^*$ strengthens the convergence of the Newton or the successive substitution methods. Unfortunately, the solution to Eq. 5 is also an optimization problem with constraints. Michelsen\textsuperscript{2} has solved the problem by locating the stationary points of the TPD function. This approach needs to solve $(n_i - 1)$ nonlinear equations. A good initial guess is required to avoid the trivial solution. Because not all stationary points can be found with this method, phase stability cannot always be guaranteed.\textsuperscript{3} Later, we will give an example of a CO\textsubscript{2}-crude system for which the approach of locating the stationary points misses the true solution in spite of its novelty and strengths.

Several methods have been proposed to improve the calculation of the TPD function. These include homotopy-continuation,\textsuperscript{4} branch and bound,\textsuperscript{5} and differential geometry, and the theory of differential equations.\textsuperscript{6}

In this paper, we calculate the multiphase equilibria by direct minimization of the Gibbs free energy. The SA algorithm is used for the minimization. We also use the SA algorithm to minimize the TPD function to test the stability of a mixture. In the following, after a brief
description of the SA algorithm and the formulation of the stability-analysis calculation, we will formulate the multiphase flash calculations. Then we will present the results by use of the SA algorithm.

**SA Algorithm**

We need to minimize the Gibbs free energy expression given by Eq. 1 subject to the constraints given by Eqs. 2 and 3 to obtain \( n_i \)'s. Finding the global minimum with constraints is, in general, a very difficult problem. Disciplines ranging from economics to engineering need to use minimization (or optimization) algorithms. Recently, the SA approach has demonstrated superiority over other optimizing methods. The approach is particularly effective when the global extremum is hidden among many local extrema.

The root of the SA algorithm is in thermodynamics. When a molten metal is cooled carefully and slowly (annealing process), the system is able to reach a highly ordered crystalline state of the lowest energy. Rapid cooling (quenching process) leads to a polycrystalline or amorphous state having somewhat higher energy. The SA algorithm is analogous to the annealing process of the molten metal. It decreases the objective function slowly to reach its global minimum. Ref. 6 provides the detailed description of the method. Mathematically, it optimizes globally an objective function with the constraints of upper and lower bounds. Refs. 7 and 8 make an extensive comparison of the SA algorithm with other optimization algorithms. It has been found that the algorithm has the following superiority:

1. It almost always finds the global minimum among many local minima.
2. The number of independent variables can be very high (as high as tens of thousands). The sole drawback to the method is the high computational cost because of the “slow cooling process.” The computing time increases linearly with the number of independent variables.

We briefly describe the algorithm in the Appendix. Refs. 7 and 8 provide a detailed description. There are various applications of the SA algorithm in science and engineering fields. We have recently used this algorithm to determine the number of asphaltene and resin molecules in a micelle. In view of our pleasant experience with the SA algorithm in the micelle work and the above features, it was appropriate to test it for complex problems in phase-behavior and stability-analysis calculations.

**Formulation of Stability-Analysis Calculations**

The chemical potential of Component \( i \) in a mixture is expressed by

\[
\mu_i = \mu_i(T) + RT \ln f_i(T)
\]

where \( \mu_i(T) \) and \( f_i(T) \) are the chemical potential and fugacity in the standard state. Introduction of Eq. 6 into Eq. 5a yields

\[
\overline{D}(\mu) = \sum_{i=1}^{n_c} \mu_i \ln f_i(\mu)/f_i(\mu)
\]

where \( \overline{D}(\mu) = D(\mu)/RT \).

From Eq. 5b, we obtain

\[
u_i = 1.0 - \sum_{i=1}^{n_c} \mu_i
\]

and then \( \overline{D}(\mu) \) is minimized with respect to independent variables \( \mu_i \) \( (i = 1, 2, \ldots, n_c - 1) \) with the SA algorithm subject to the constraints

\[
0 \leq \mu_i \leq 1(i = 1, 2, \ldots, n_c - 1).
\]

The optimized value, \( \overline{D}(\mu) \), provides the stability analysis of the mixture, and the optimized \( n_i \) can be used for the initial composition of the incipient phase for the following phase-splitting calculations.

**Formulation of Multiphase-Equilibrium Calculations**

The Gibbs free energy of the system sketched in the right side of Fig. 1 is given by

\[
G = \sum_{j=1}^{n_p} \sum_{i=1}^{n_j} n_{ij} \mu_i
\]

where \( \mu_i \) is given by Eq. 6. Combining Eqs. 6 and 11 leads to

\[
G = \sum_{i=1}^{n_c} n_i \mu_i(T) + RT \sum_{j=1}^{n_p} \sum_{i=1}^{n_j} n_{ij} \ln f_i(T)
\]

In Eq. 12, the first term on the left side is a constant and the second term is a function of \( n_i \) \( (i = 1, 2, \ldots, n_c; j = 1, 2, \ldots, n_p) \); therefore, there are \( n_c \times n_p \) variables. We can eliminate the mole numbers of one phase (say, Phase 1) from the material balance constraint, Eq. 2:

\[
n_{ij} = n_i - \sum_{j=1}^{n_j} n_{ij}(i = 1, 2, \ldots, n_c)
\]

The minimization of \( G \) with the constraints

\[
0 \leq n_{ij} \leq n_i(i = 1, 2, 3, \ldots, n_c; j = 2, 3, \ldots, n_p)
\]

provides \( n_{ij}(i = 1, 2, \ldots, n_c; j = 1, 2, \ldots, n_p) \). The minimization is performed with the SA algorithm.

**Results**

In the following, a number of complex phase-equilibrium calculations are performed to demonstrate the reliability of the SA minimization algorithm. In all calculations, we use the Peng-Robinson equation of state (PR-EOS).

**Vapor-Liquid-Equilibrium (VLE) Calculations in the Critical Region**

To examine the phase-equilibrium calculations in the near-critical regions, two mixtures are selected. Outside the critical region one may use the Wilson correlation,

\[
K_i = y_i/x_i = \frac{P_c}{P_v} \exp[5.37(1 + \omega_i)(1 - T_c/T)]
\]

for the initial guess. Note that \( y_i \) and \( x_i \) represent the gas and liquid, and feed mole fractions, respectively; \( y_i = n_i^g/\sum_{i=1}^{n_c} n_i^g \), \( x_i = n_i^l/\sum_{i=1}^{n_c} n_i^l \). In the critical region, our initial guesses are \( K_i = 1.0 \) for \( C_1 \), \( C_2 \), \( C_3 \), \( N_2 \), and \( CO_2 \) and \( K_i = 0.5 \) for the other components. There is no need to generate initial \( K_i \) values from the stability-analysis calculations. The SA searches for the optimized point randomly. Therefore, the computational time is nearly the same for the near-critical and away from the critical region.
**TABLE 1—COMPOSITION OF THE SYNTHETIC-OIL AND THE CO2-HYDROCARBON INTERACTION COEFFICIENTS**

<table>
<thead>
<tr>
<th>Component</th>
<th>( z_i ) mol%</th>
<th>( k_{i, CO_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>35</td>
<td>0.085</td>
</tr>
<tr>
<td>CO2</td>
<td>3</td>
<td>0.090</td>
</tr>
<tr>
<td>C3</td>
<td>4</td>
<td>0.095</td>
</tr>
<tr>
<td>n-C4</td>
<td>6</td>
<td>0.10</td>
</tr>
<tr>
<td>n-C5</td>
<td>4</td>
<td>0.10</td>
</tr>
<tr>
<td>n-C6</td>
<td>3</td>
<td>0.105</td>
</tr>
<tr>
<td>n-C7</td>
<td>5</td>
<td>0.105</td>
</tr>
<tr>
<td>n-C8</td>
<td>5</td>
<td>0.105</td>
</tr>
<tr>
<td>n-C10</td>
<td>30</td>
<td>0.105</td>
</tr>
<tr>
<td>n-C14</td>
<td>5</td>
<td>0.105</td>
</tr>
</tbody>
</table>

**C1/n-C4/n-C10 Mixture.** The interaction coefficients for the PR-EOS are set to \( k_{C_1/C_4} = 0.012 \), \( k_{C_1/C_{10}} = 0.04 \), and \( k_{C_4/C_{10}} = 0.010 \). We performed the VLE computations at 344.15 K and 207 bar for the mixture and the phase envelope was constructed to the critical point.

**Synthetic Oil-CO2 Mixture.** The VLE of the synthetic oil (Table 1 lists the composition) and CO2 mixture is also calculated. Table 1 also lists the interaction coefficients between CO2 and hydrocarbons. The values between hydrocarbons are estimated from Ref. 12.

\[
k_0 = 1.0 - \left( \frac{2V_i^{1/3}V_j^{1/3}}{V_i^{1/3} + V_j^{1/3}} \right) \theta \quad \text{(16)}
\]

where \( V_c \) is the critical volume. The parameter \( \theta \) is set equal to 0.9.

**Fig. 2A** shows the calculated phase-equilibrium constants, \( K_i \) vs. CO2 concentrations at \( T = 322 \) K and \( p = 105.35 \) bar. **Fig. 2B** shows the enlarged \( K \)-values for C1 and n-C14 near the critical point. The results clearly reveal that the SA algorithm can find the global minimization very close to the critical point.

We also used a commercial software that uses the stability-analysis and fugacity-equality criteria. In the case of C1/n-C4/n-C10, the commercial software was able to do all calculations to the critical point, as did the SA algorithm. However, for the synthetic oil-CO2 mixture, the commercial software computed the \( K \)-values, which are several times larger than our results and the experimental data.

The commercial software uses the successive substitution in combination with Newton method. The initial guess could be one reason for the unreliable results.

**Vapor-Liquid-Liquid-Equilibrium (VLLE) Calculations**

In VLLE calculations, one can use the light liquid phase (say phase 1) as the reference phase. The initial estimation of the \( K \)-values can be made from

\[
K_i^1 = y_i/x_i = \phi_i^1(x^1)/\phi_i^1 \quad \text{(17a)}
\]

and

\[
K_i^2 = x_i^2/x_i = \phi_i^2(x^2)/\phi_i^2 \quad \text{(17b)}
\]

suggested in Ref. 13. In these equations, \( \phi_i^1 \) and \( \phi_i^2 \) are the fugacity coefficients of pure Component \( i \) in the vapor and liquid states, respectively. The composition of the reference phase (i.e., Phase 1) is assumed to be the feed composition, \( x^1 \). Using the above initial estimation, three-phase flash calculation can be performed when the amount of all phases is not very small. When the amount of one phase among these phases is very small (close to a phase boundary), \( K_i^1 \) and \( K_i^2 \) values from the two-phase flash and stability-analysis calculations are required to guarantee the correct three-phase flash calculations. For this purpose, Michelsen's stepwise approach can be used. First, a VL two-phase flash is performed. Then, the composition of each phase is tested for stability. In the stability-analysis calculations, the initial estimations from Eqs. 17a and 17b are used for the VL and LL phase split. In this case, \( x^2 \) in Eq. 17 represents the composition to be tested for stability. The approximate composition of the incipient phase is obtained by the stability-analysis calculation. The initial compositions of the three-phases are generated from the VL flash calculations and stability analysis. The following examples are typical three-phase systems encountered: H2S-containing and CO2-containing reservoir fluid mixtures.

**Sour-Gas System:** Robinson et al.\(^{15} \) observed the liquid-phase split at low temperatures for sour-gas mixtures. Using the VLLE algorithm, the equilibrium state of the sour-gas system (Table 2 lists the composition) is computed at desired temperatures and pressures. The interaction coefficients between hydrocarbons are estimated with Eq. 16 with \( \theta = 1.5 \). Table 2 lists other interaction coefficients. Because the amount of the H2S-rich liquid phase for the sour-gas mixture was very small at 21.9 bar and 178.8 K, Robinson et al.\(^{15} \) could not measure the composition of that phase. **Fig. 3** depicts the calculated phase amounts vs. temperature at 178.8 K. The system changes from only one vapor phase at 1.0 bar into VLL phases at 1.4 bar. **Fig. 3** shows that the amount of the H2S-rich liquid is very small in a wide pressure range, in line with experimental observations.
### Table 2: Composition and Nonhydrocarbon-Hydrocarbon Interaction Coefficients for the Sour-Gas System

<table>
<thead>
<tr>
<th>Component</th>
<th>$z_{mol%}$</th>
<th>$k_{i-N_2}$</th>
<th>$k_{i-CO_2}$</th>
<th>$k_{i-C_6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>7.026</td>
<td>-0.02</td>
<td>0.120</td>
<td>0.080</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>70.592</td>
<td>0.200</td>
<td>0.126</td>
<td>0.078</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>1.966</td>
<td>0.031</td>
<td>0.135</td>
<td>0.125</td>
</tr>
<tr>
<td>C$_1$</td>
<td>6.860</td>
<td>0.042</td>
<td>0.150</td>
<td>0.080</td>
</tr>
<tr>
<td>C$_2$</td>
<td>10.559</td>
<td>0.091</td>
<td>0.150</td>
<td>0.080</td>
</tr>
<tr>
<td>C$_3$</td>
<td>2.967</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### C$_1$/CO$_2$n-C$_{16}$ Mixture

CO$_2$-hydrocarbon mixtures of high CO$_2$ concentration may have a three-phase region. The interaction coefficients for this ternary mixture used in the PR-EOS are $k_{C_1/CO_2} = -0.100$, $k_{C_1/C_6} = -0.078$, and $k_{CO_2/C_6} = 0.125$. Fig. 4A shows the calculated amount of each phase vs. pressure at $T = 294.3$ K for $z_{C_1} = 5\%$, $z_{CO_2} = 90\%$, and $z_{C_6} = 5\%$ (mole).\[\text{Fig. 4B shows the predicted amounts of phases vs. CO}_2\text{concentrations at T = 294.3 K and p = 70 bar; in this mixture, z}_{C_1} = z_{C_6}.\]

#### CO$_2$-Reservoir Oil System

The recombined oil B and CO$_2$ mixture investigated by Shelnor and Yarbrough is used for the three-phase flash calculations. The C$_{18}$ is split into seven pseudocomponents, which Table 3 lists. Cavett's correlations are used to calculate the critical properties and acentric factors of these pseudocomponents. Table 3 lists the interaction coefficients between CO$_2$-hydrocarbons and N$_2$-hydrocarbons. The interaction coefficients between hydrocarbon hydrocarbon species are estimated by use of Eq. 16 with $\theta = 0.90$. Fig. 5 shows the calculated phase amounts vs. pressure. The interaction coefficients between CO$_2$-hydrocarbons have a strong effect on the three-phase region. The predicted compositions at 207.6 K and 81.0 bar are in good agreement with the experimental data except for the C$_{18}$. By adjusting the CO$_2$-crude residue interaction coefficient, one may improve the predicted value of the C$_{18}$ residue.

For the C$_1$/CO$_2$/n-C$_{16}$ mixture and the sour-gas system described previously, both the SA algorithm and the commercial software give the same results. However, for the CO$_2$-crude mixture, the predicted amount of the phases and the three-phase region are indeed different. The calculated Gibbs free energy of the system that Fig. 5 represents is less than that computed by the commercial software at all the pressures.

#### Vapor-Liquid-Solid-Equilibrium (VLSE) Calculations

Recently, we used the multisolid concept to describe the wax precipitation in petroleum fluids. Our work is limited to liquid-multisolid equilibrium calculations. One may use the ideas presented here to perform vapor-liquid-multisolid equilibrium computations. Fig. 6 schematically shows the vapor-liquid-multisolid flash process. The solid phases are assumed to be pure, and, therefore, the calculations are expected to perform very smoothly. The initial estimation from Eq. 15 is used for VL phases. Because of the pure state, the initial estimates for solid phases are not required. We will present three examples for the VL-multisolid equilibrium calculations. Ref. 19 provides the critical and other properties of various hydrocarbon groups. The
TABLE 3—COMPOSITION OF CO₂-RESERVOIR OIL MIXTURE AND THE CO₂-HYDROCARBON AND N₂-HYDROCARBON INTERACTION COEFFICIENTS

<table>
<thead>
<tr>
<th>Component</th>
<th>M</th>
<th>( z_i )</th>
<th>( k_{i-CO₂} )</th>
<th>( k_{i-N₂} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>78.95</td>
<td>0.10</td>
<td>-0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>N₂</td>
<td>0.10</td>
<td>3.44</td>
<td>0.075</td>
<td>0.08</td>
</tr>
<tr>
<td>C₁</td>
<td>0.85</td>
<td>0.63</td>
<td>0.080</td>
<td>0.07</td>
</tr>
<tr>
<td>C₂</td>
<td>0.63</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>C₃</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>i-C₄</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>n-C₄</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>i-C₅</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>n-C₅</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>C₆</td>
<td>0.085</td>
<td>0.085</td>
<td>0.85</td>
<td>0.07</td>
</tr>
<tr>
<td>CP₁</td>
<td>112.8</td>
<td>3.82</td>
<td>0.095</td>
<td>0.10</td>
</tr>
<tr>
<td>CP₂</td>
<td>161.2</td>
<td>3.46</td>
<td>0.095</td>
<td>0.12</td>
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<tr>
<td>CP₃</td>
<td>223.2</td>
<td>2.64</td>
<td>0.095</td>
<td>0.12</td>
</tr>
<tr>
<td>CP₄</td>
<td>304.4</td>
<td>2.01</td>
<td>0.095</td>
<td>0.12</td>
</tr>
<tr>
<td>CP₅</td>
<td>417.5</td>
<td>1.22</td>
<td>0.095</td>
<td>0.12</td>
</tr>
<tr>
<td>CP₆</td>
<td>636.8</td>
<td>0.69</td>
<td>0.095</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Interaction coefficients are estimated from Eq. 16 with \( \theta = 1.0 \). The amount of the precipitated solid is obtained from

\[
\text{Wt\%} = 100.0 \left( \frac{\sum n_i \times M_i}{\sum \left( n_i + n_i^* \right) \times M_i} \right) \]

C₄/n-C₅/n-C₂₀/n-C₃₀ Mixture. The feed composition of the mixture is 50, 35, 10, and 5 moles of C₁, n-C₅, n-C₂₀, and n-C₃₀, respectively. Fig. 7 shows the calculated wax amount vs. temperature at \( p = 50 \) bar. The cloudpoint temperature of the mixture is 317 K. When the temperature is higher than 290 K, only n-C₂₀ is in the solid state. The solid phase of n-C₂₀ appears at about 290 K.

C₄/Model Synthetic Oil Mixture: Pan et al.¹⁹ used a model synthetic oil to study wax composition. The mixture of 50% (mole) of methane and the model synthetic oil is used to perform VLS calculations. Fig. 8 shows the precipitated solid amount vs. temperature at \( p = 50 \) bar. The cloudpoint temperature of the mixture is about 329 K.

Reservoir Oil. The reservoir oil, Oil 1 from Ref. 19, is used to perform the VLS calculations. The composition of the reservoir fluid and the characterization of C₄₀ can be found in Ref. 19. We performed the VLS calculation at 270 K and 60 bar. The calculated amount (mole%) of vapor, liquid, and solids is 9.2, 90.7, and 0.1, respectively. The precipitated species are P-CP₁, N-CP₁, P-C₃₅₋₄, and P-C₅₀, and the amount (wt%) of those precipitated species are 0.003, 0.367, 0.05, and 0.028, respectively. When there is no gas phase, the results from the SA algorithm and the conventional approach are the same, as expected.

Concluding Remarks

Multiphase equilibrium computations can be performed very reliably by direct minimization of Gibbs free energy by use of the powerful algorithm of simulated annealing. The stability analysis can also be calculated with the same algorithm. The SA algorithm can escape the local minima and converge to the global minimum; therefore, the method is very reliable. For all the examples we tested, the method works well. Because the conventional methods of multiphase-equilibrium calculations do not enjoy such a high reliability, the SA algorithm becomes very attractive. The method is, however, costly in computational time. Computer power is increasing rapidly and, therefore, the cost will decrease in the future.

The SA searches for the minimization by random movement. Therefore, the algorithm has nearly the same efficiency and reliability for the calculations in the near-critical region and away from the critical region.

We used the SA algorithm for single flashes and not in a compositional model because of the high cost of computing time. However, in the simulation models, SA can be used as a diagnostic tool.

The computational time for the SA algorithm does not depend on the distance to the critical point, while for the conventional approach, it does. From limited runs, we can state that minimization of Gibbs free energy with the SA algorithm could be one to two orders of magnitude slower than the conventional approach.

Acknowledgment

This work was supported by the members of the Reservoir Engineering Research Inst. Their support is greatly appreciated.

Nomenclature

\( D \) = tangent-plane distance function defined in Eq. 5a
\( \gamma \) = fugacity
\( G \) = total Gibbs free energy

![Fig. 5—Mole percent of different phases vs. pressure for the CO₂-reservoir oil system at 307.6 K.](image)

![Fig. 6—Schematic representation of the vapor-liquid-multisolid phase flash process.](image)
Fig. 7—Predicted solid amount vs. temperature for the \( C_1/n-C_9/n-C_{20}/n-C_{30} \) mixture at 50 bar.

Fig. 8—Predicted solid amount vs. temperature for the \( C_1 \) model synthetic oil mixture at 50 bar.

\[ n_c = \text{number of components} \]
\[ n_p = \text{number of phases} \]
\[ K = \text{phase-equilibrium constant} \]
\[ k = \text{binary-interaction coefficient} \]
\[ M = \text{molecular weight} \]
\[ n = \text{mole number} \]
\[ p = \text{pressure (bar)} \]
\[ P = \text{defined in Eq. A2} \]
\[ R = \text{universal gas constant} \]
\[ T = \text{temperature (K)} \]
\[ V = \text{volume} \]
\[ u = \text{mole fraction} \]
\[ w = \text{mole fraction} \]
\[ s = \text{mole fraction in vapor phase} \]
\[ y = \text{mole fraction in liquid phase} \]
\[ z = \text{mole fraction in feed} \]
\[ \theta = \text{defined in Eq. 16} \]
\[ \mu = \text{chemical potential} \]
\[ \phi = \text{fugacity coefficient} \]
\[ \omega = \text{acentric factor} \]

\textbf{Superscripts}

\[ L = \text{liquid} \]
\[ S = \text{solid} \]
\[ V = \text{vapor} \]
\[ * = \text{optimized value} \]
\[ l = \text{light liquid} \]
\[ h = \text{heavy liquid} \]
\[ 0 = \text{standard state} \]

\textbf{Subscripts}

\[ c = \text{critical} \]
\[ i = \text{index of Component} \]
\[ f = \text{index of Phase} \]

\textbf{Symbols}

\[ \text{— = \text{vector}} \]

\textbf{References}

Appendix—Simulated Annealing Algorithm

In this work, we used the SA algorithm proposed by Corana et al.7 and modified by Goffe et al.8 The detailed description can be found in these two papers.

Let $\mathbf{x}$ be a vector of $N$ dimensions: $(x_1, x_2, \ldots, x_N)$ are its components. Let $f(\mathbf{x})$ be the function to be minimized. Let $a$ and $b$ be the lower and upper bounds of $x_i$, i.e., $a_1 < x_1 < b_1, a_2 < x_2 < b_2, \ldots, a_N < x_N < b_N$. The following starting parameters are required for the minimization:

- $\mathbf{x}_0$—starting point vector
- $v_0$—starting step vector
- $T_0$—starting temperature
- $\varepsilon_c$—step adjustment vector
- $a$—lower bound vector
- $b$—upper bound vector
- $RT$—temperature reduction factor
- $\varepsilon_t$—error tolerance for termination
- $n_0$—number of cycles before the step is adjusted
- $n_t$—number of iterations before temperature is reduced
- $n_\text{max}$—number of successive temperature reductions to test for termination.

First, a function evaluation is made at $x_0$ and its value $f_0$ is recorded. In the second step, along each coordinate direction (i.e., the following computation of acceptance and rejection of the point is performed for each component $x_i$ of $\mathbf{x}$), a new value is calculated from

$$x'_i = x_i + rv_i, \quad \ldots \quad (A-1)$$

where $r$ is a uniformly distributed random number in the range $[-1,1]$, and $v_i$ is the $i$th element of the step vector $\mathbf{v}$. The $x'_i$ denotes the point $(x_1, x_2, \ldots, x'_i, \ldots, x_N)$. If the function at the point $f'_i$ is less than $f$ (the latest value), $x'_i$ is accepted, and $x_i$ and $f$ are updated with $x'_i$ and $f'_i$. If $f'_i$ is greater than $f$, the Metropolis criterion is used to calculate the acceptance probability of the point from

$$P = \exp\left(\frac{f - f'}{T}\right), \quad \ldots \quad (A-2)$$

At the same time, a uniformly distributed random number $P'$ is generated from $[0,1]$. If $P' < P$, then the point is accepted, and $x_i$ and $f$ are updated with $x'_i$ and $f'$. Otherwise, the point is rejected.

After $n_0$ steps, the step vector $\mathbf{v}$ is updated by

$$v'_i = v_i \left(1 + c_i \frac{n_0/n_i - 0.6}{0.4}\right) \text{if } n_0/n_i > 0.6 \quad \ldots \quad (A-3a)$$

$$v'_i = v_i \left(1 + c_i \frac{0.4 - n_0/n_i}{0.4}\right) \text{if } n_0/n_i < 0.4 \quad \ldots \quad (A-3b)$$

Otherwise,

$$v'_i = v_i \quad \ldots \quad (A-3c)$$

where $n_0$ is the number of the acceptance points. Using Eq. A3, 50% of all moves are accepted. Ref. 7 gives a detailed explanation for the relation between Eq. A3 and the acceptance percentage and the reason why the acceptance rate is 50%.

After $n_0$ loops for the step vector adjustments, the temperature is reduced. The new temperature is given by

$$T = RT \times T, \quad \ldots \quad (A-4)$$

where $RT$ is in $(0,1)$.

If the termination criterion is satisfied, the algorithm terminates; otherwise, one goes to the next step, and the computation goes on until the termination criterion is satisfied. Fig. A1 shows a block diagram for the SA algorithm.

The parameter values suggested in Ref. 7 are $n_0 = 20, n_t = \max(100, 5 \times N), c_2 = 2.0, i_1 = 1, i_2 = 2, \ldots, N, n_i = 4$, and $RT = 0.85$.

We found that the $n_0$ parameter has a significant effect on the computational time, and the value given by Ref. 8 is too high. A high $n_0$ value can make the SA more robust, but the computational time increases dramatically. Therefore, a reasonable value of $n_0$ is the key for robustness and cost of the SA algorithm. In our computation, $n_0$ is set in the range of $[5,10]$. Another important parameter is the starting temperature $T_0$. It varies with the objective function, and we set $T_0 = 5.0$. All other parameter values proposed by Ref. 8 are used in this study.

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**SI Metric Conversion Factors**

<table>
<thead>
<tr>
<th>bar $\times 1.0^9$</th>
<th>E+05 $= \text{Pa}$</th>
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<tbody>
<tr>
<td>$^\circ\text{F}$ $\left(^\circ\text{C} + 459.67\right)/1.8$</td>
<td>$= K$</td>
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</tbody>
</table>

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