

1. Introduction

In the recent years, with advances in computing technologies and statistical mechanics, the molecularly based equations of state like SAFT (statistical associated fluid theory)¹⁻⁵ have become increasingly popular tools for modeling the phase behavior, particularly for the system involving the associating or the chainlike molecules. It is often found difficult to calculate the phase behavior reliably from even a relatively simple equation of state. Since the number of phases is not known priori, the two stage strategy is often followed to compute the phase equilibrium. First, for the given feed composition and for the fixed temperature and pressure, the phase split problem is solved, which determines whether the considered mixture will split into two different phases. The second step is the phase split problem which determines the compositions of the known number of phases. Once the phase split problem is solved, the two phases are then checked for the phase stability. If phase instability is encountered, the phase split problem is solved again to obtain an improved bound on total Gibbs energy of the system either with same number of phases or with increased number of phases.

Reliable computation of the phase equilibrium is equivalent to finding the global minimum of the total Gibbs free energy of the system. It is shown that the phase stability analysis is equivalent of the global optimality test that determines whether the phase being tested corresponds to the global minimum of the total Gibbs free energy. If it is found that the phase is not stable, the phase split calculations are performed which seeks the local minimum of the Gibbs free energy of the system. The number of phases is changed and the phase stability and phase split calculations are repeated until all the phases are found stable with respect to the phase stability test. Clearly, the phase stability calculations have to be performed globally to obtain the solution corresponding to the global minimum of the Gibbs free energy. Conventional initialization dependent techniques can often fail to compute the global minimum of the phase stability problem. Hence there has been significant interests towards development of methods that are more reliable. McDonald and Floudas⁶⁻⁷ have found that the phase stability problem can be reformulated using convex underestimating functions for activity coefficient models and EOS models that can be solved with mathematical guarantee using the branch and bound method. Interval analysis is another approach which gives mathematical and computational guarantee of the global optimum solution. Xu and Stadtherr⁸ have applied the interval based method to reliably compute the phase stability and the phase equilibrium from SAFT equation of state. Although the method is completely reliable, the computation time is required for the phase stability and the phase equilibrium computations are high even for binary system and can increase further as the number of components increases.

An alternative approach to solve the phase stability problem globally is the use of the homotopy continuation method. Sun and Seider⁹ have shown that all the for the activity coefficient models and cubic EOS models, all the solutions of the phase stability problem can be found out if the homotopy path is started using the well chosen initial points. We demonstrate here the use of the homotopy continuation method to reliably compute the

phase stability and the phase equilibrium problems for the SAFT equation of state models.

2. Problem Formulation

2.1 SAFT equation of state.

For multicomponent system Huang and Radosz⁴ proposed,

$$a^{res} = a^{hs} + a^{dis} + a^{chain} + a^{assoc}$$

The hard sphere contribution a^{hs} is based on the hard sphere equation of state and is given by

$$\frac{a^{hs}}{RT} = \frac{6}{\pi N_A \rho} \left[\frac{\xi_2^3 + 3\xi_1 \xi_2 \xi_3 - 3\xi_1 \xi_2 \xi_3^2}{\xi_3 (1 - \xi_3)^2} - \left(\xi_0 - \frac{\xi_2^3}{\xi_3^2} \right) \ln(1 - \xi_3) \right]$$

$$\text{Where } \xi_j = \frac{\pi N_A \rho}{6} \sum_{i=1}^N x_i m_i d_{ii}^j \quad j = 0,1,2,3$$

Here, ρ is the total molar density of the mixture, x_i is the mole fraction of the component i , N is the total number of component in the mixture, N_A is Avogadro's number. d_{ii} is the temperature dependent segment diameter that is given by

$$d_{ii} = \sigma_i \left[1 - 0.12 \exp\left(-\frac{3u_0}{kT}\right) \right]$$

$$\text{Where } \sigma_i = \left(v_i^{00} \frac{6\tau}{\pi N_A} \right)^{1/3}$$

Here k is Boltzmann's constant and $\tau = \frac{\pi\sqrt{2}}{6}$ is the packing fraction for closed packed spheres. The dispersion term a^{dis} used by Huang and Radosz³⁻⁴ is given by

$$\frac{a^{dis}}{RT} = m \sum_{i=1}^4 \sum_{j=1}^9 D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j$$

Where

$$m = \sum_{i=1}^N x_i m_i$$

$$\eta = \frac{\pi N_A \rho}{6} \sum_{i=1}^N x_i m_i d_{ii}^3 = \xi_3$$

$$\frac{u}{kT} = \frac{\sum_{i=1}^N \sum_{j=1}^N x_i x_j m_i m_j v_{ij}^0 (u_{ij} / kT)}{\sum_{i=1}^N \sum_{j=1}^N x_i x_j m_i m_j v_{ij}^0}$$

$$\text{Where } v_{ij}^0 = \left[\frac{(v_i^0)^{1/3} + (v_j^0)^{1/3}}{2} \right]^3$$

$$u_{ij} = (1 - k_{ij}) (u_{ii} u_{jj})^{1/2}$$

$$v_i^0 = v_i^{00} \left[1 - 0.12 \exp\left(\frac{-3u^0}{kT}\right) \right]^3$$

$$\text{And } u_{ii} = u_i^0 \left(1 + \frac{e}{kT} \right)$$

D_{ij} represents the Chen and Kreglewski¹¹ constants. The k_{ij} are binary interaction parameters that can be fit to the experimental data.

The chain term is given by

$$\frac{a^{chain}}{RT} = \sum_{i=1}^N x_i (1 - m_i \ln(g_{ii}^{hs}(d_{ii})))$$

$$\text{Where } g_{ii}^{hs}(d_{ii}) = \frac{1}{1 - \xi_3} + \frac{3d_{ii}}{2} \frac{\xi_2}{(1 - \xi_3)^2} + 2 \left(\frac{d_{ii}}{2} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^2}$$

The more general correlation function is

$$g_{ii}^{hs}(d_{ii}) = \frac{1}{1 - \xi_3} + \frac{3d_{ii} d_{jj}}{d_{ii} + d_{jj}} \frac{\xi_2}{(1 - \xi_3)^2} + 2 \left(\frac{d_{ii} d_{jj}}{d_{ii} + d_{jj}} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^2}$$

The association term is expressed as

$$\frac{a^{assoc}}{RT} = \sum_{i=1}^N x_i \left[\sum_{A_i} \left(\ln X^{A_i} - \frac{X^{A_i}}{2} \right) + \frac{M_i}{2} \right]$$

Where summation over A_i indicates summation over all association sites over component i . M_i is number of association sites on component i . X^{A_i} is the mole fraction of molecules of i that are not bonded at the association site A_i which can be determined from

$$X^{A_i} = \left[1 + N_A \sum_{j=1}^N \sum_{B_j} \rho_j X^{B_j} \Delta^{A_j B_j} \right]^{-1}$$

Where the summation over B_j gives summation over all association sites on component j . $\Delta^{A_j B_j}$ is the association strength function that is given by

$$\Delta^{A_j B_j} = g_{ij}^{hs}(d_{ij}) \left(\exp(\epsilon^{A_j B_j} / kT) - 1 \right) \sigma_{ij}^3 k^{A_j B_j}$$

Where $\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2}$

The equation of state is written as

$$P = \rho^2 \left(\frac{\partial a^{res}(x, \rho)}{\partial \rho} \right)_{x,T} + \rho RT$$

Here, the last term in equation indicates the ideal gas contribution.

2.2 Phase stability and phase split

The volume based approach proposed by Nagaragen et al.¹¹ is used to formulate the phase stability problem. Based on their approach, the tangent plane distant function is given by

$$D(\rho) = a(\rho) - [a(\rho_0) + \nabla a(\rho_0) \cdot (\rho - \rho_0)]$$

A given mixture at constant temperature and pressure and composition ρ_0 is stable if Helmholtz energy density function $a(\rho)$ doesn't fall below the plane tangent to the surface

at ρ_0 . The stationary conditions of the optimization problem form the following nonlinear equations.

$$\nabla a(\rho) - \nabla a(\rho_0) = 0$$

As stated earlier, the phase split problem is solved locally for different initial guess. The phase stability roots are provided as an initial guess for the phase split problem. The phase split problem can be formulated by equating the fugacity of the component in each phase.

$$f_j^i = f_j^i$$

$$P = (\rho^2)^i \left(\frac{\partial a^{res}(x, \rho)}{\partial \rho} \right)_{x,T}^i + \rho RT$$

$$(\sum x)^i - 1 = 0$$

Here, the subscript j indicated the component and the superscript i indicated the phase.

3. Problem solving methodology.

For finding the density roots and for phase stability computations, the Newton based homotopy continuation method is applied. The phase split problem is solved locally using trust region dogleg approach. While modeling associating compounds, internal variables are solved locally during each function evaluation. The stepwise procedure followed for the phase equilibrium computations can be summarized as follows.

1. For the given feed composition, temperature and pressure, find all the density roots by homotopy continuation method.
2. Find the root corresponding to the minimum Gibbs free energy
3. Solve the phase stability problem globally using homotopy method for each phase.
4. Compute tangent plane distance to determine the phase stability
5. If given phase is not stable, increase the number of phases by one and perform phase split computations locally with the initial guess provided by the phase stability roots. If each phase is found stable, out put the results and exit.
6. If the improved bound on Gibbs free energy is not found then solve the phase split problem with another guess
7. Once the improved bound on Gibbs free energy is found, go to 3.
8. Repeat procedure until all the phases present are stable.

4. Test problems and results

To compare our results and computation time with those obtained by interval method, the binary test systems selected are same as Xu and Stadtherr⁸. For all the test problems, the SAFT parameters used for each component are taken from Huang and Radosz.⁴

Problem 1. (self associating type 1A)

The mixture of acetic acid (1) and benzene (2) belongs to this category. Benzene has no association site while acetic acid molecule self associates. Fig. 1 and Fig. 2 show the homotopy path for the density roots and the phase stability. Table 1 shows summary of the results.

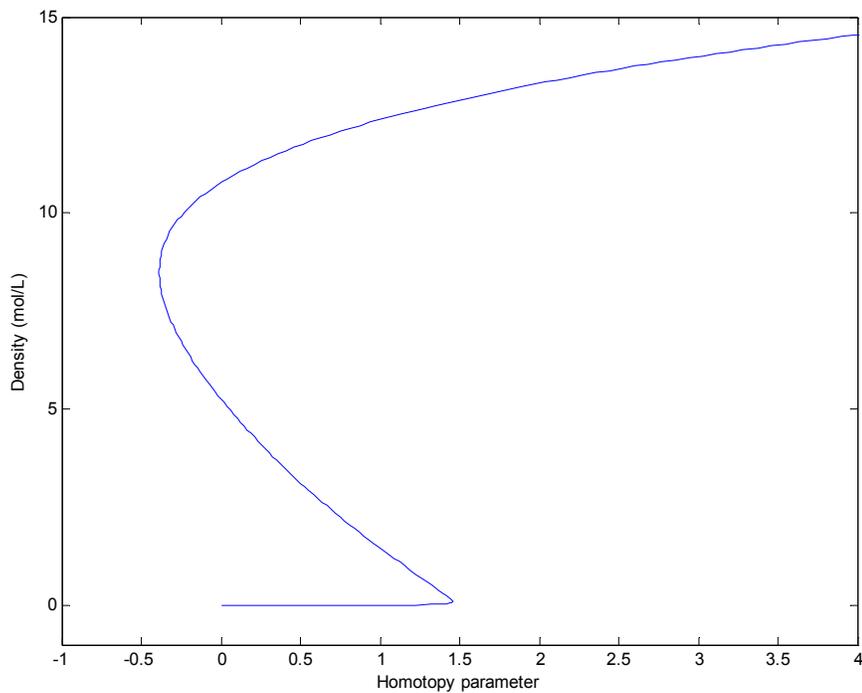


Fig. 1. Homotopy path for the computation of density roots

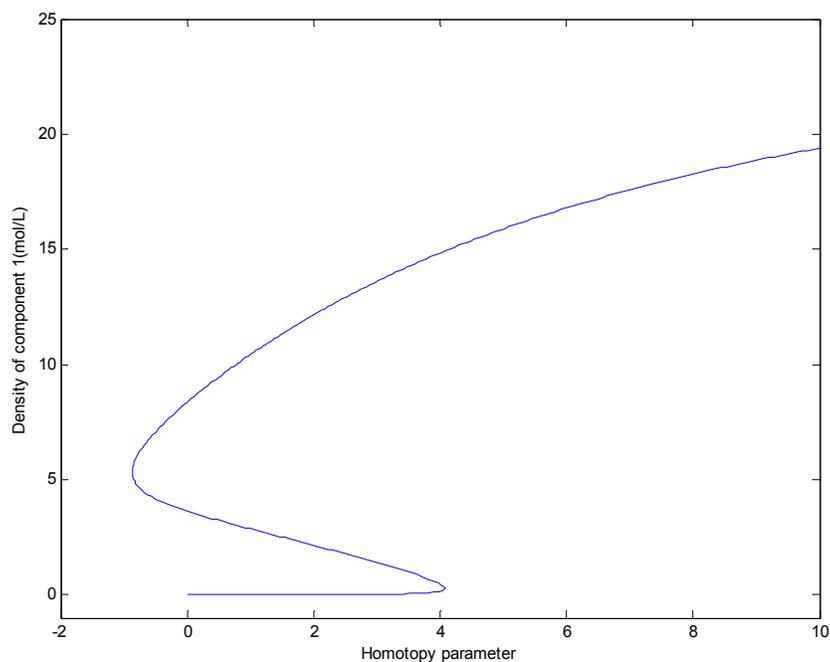


Fig. 2. Homotopy path for the computation of phase stability

Table 1.

Feed Composition	Density roots	Phase stability roots	TPD	Phase I	Phase II	Total CPU time s
0.25, 0.75	0.0097 ^g , 1.4634, 12.3842	0.0024, 0.0073 3.0134, 2.7623 10.9250, 4.0754	0 9.2297, -0.4671	0.2379 0.7621 0.0096	0.7057 0.2943 14.8235	182

Superscript g indicates the root corresponding to the minimum Gibbs free energy.

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