

A Survey on Phase Stability Analysis of Liquid Mixtures using Interval Newton Bisection Algorithm, NRTL Model, SAFT EOS Method

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Abstract

The phase stability and phase split problems can be formulated as minimization problems, or as equivalent nonlinear equation solving problems. There are several versions of this two-stage approach. With the choice of the proper thermodynamic state functions, the two stage framework can be applied to phase equilibrium problems with various types of specifications (e.g. Constant temperature and pressure, constant temperature and density, isentropic, isenthalpic, etc.).

For determining phase equilibrium at constant temperature and pressure, the case considered here minimum in the total Gibbs energy of the system. Phase stability analysis may be interpreted as a global optimality test that determines whether the phase being tested corresponds to a global minimum in the total Gibbs energy of the system. An alternative approach for solving the phase stability problem is the use of interval analysis which uses an interval Newton/generalized bisection algorithm, NRTL Model and SAFT method.

Key Words: Phase Stability, Interval Analysis, Interval Newton/Generalised Bisection Algorithm, SAFT method.

Introduction

In liquid mixtures, the phase splitting is related to thermodynamic stability of the system which comprises information for the projection, modelling and simulation of industrial processes that involve liquid phase separation. Phase stability analysis allows determination of the exact number of coexisting phases in stable equilibrium and also provides estimation of phase compositions, affording a suitable initialization for phase equilibrium calculations. In fluid mechanics, stable flow is best described as flow that will be maintained

in spite of small disturbances or perturbations to the flow. The flow is unstable if a small disturbance will lead to the flow to progressively depart from the initial base state.

In stability theory, flow behaviour is first investigated by performing a linear stability analysis of steady state solutions satisfying appropriate equations of motion and boundary conditions. The stability of such a system is determined by examining its reaction to all possible infinitesimal disturbances to basic steady flow. These results provide the groundwork for further investigation of development of instabilities and evolution of unstable waveforms. Since these methods of analysis involve the linearization and numerical integration of nonlinear partial differential equations of motion.

The phase equilibrium modelling is essential in the design, operation, optimization and control of separation schemes. Phase behaviour of multi-component systems has great impact on process design including energy and equipment costs of separation and purification strategies. Phase equilibrium calculations are usually executed thousands of times in process simulators which becomes important in chemical, petroleum, petrochemical, pharmaceutical and other process industries where separation units are the core of process performance. Hence, these calculations must be performed reliably and efficiently, to avoid uncertainties and errors in process design.

Global optimization problems has three applications: (i) phase stability analysis, (ii) Gibbs free energy minimization and (iii) estimation of parameters in thermodynamic models.

The optimization problems of these applications can be defined as follows:

Minimize $F_{obj}(\mathbf{u})$ subject to $h_j(\mathbf{u}) = 0$ for $j = 1, 2, \dots, m$ and $\mathbf{u} \in \Omega$

where \mathbf{u} is a vector of n continuous variables in the domain $\Omega \in \mathbb{R}^n$, m is the number of equality constraints arising from the specific thermodynamic application, and $F_{obj}(\mathbf{u}) : \Omega \rightarrow \mathbb{R}$ is a real valued function. The domain Ω is defined by the upper and lower limits of each decision variable.

Phase Stability Analysis

The phase stability is determined using tangent plane analysis. A phase at specified T , P , and feed mole fraction \mathbf{z} is unstable if the Gibbs energy of mixing versus composition surface $m = \Delta g^M/RT_{\text{ever}}$ falls below a plane tangent to the surface at \mathbf{z} . That is, if the tangent plane distance

$$D(\mathbf{x}) = m(\mathbf{x}) - m_0 - \sum_{i=1}^n \left(\frac{\partial m}{\partial x_i} \right)_0 (x_i - z_i) \quad (1)$$

If Equation (1) is negative, for any composition \mathbf{x} , the phase is unstable. The subscript ‘0’ indicates evaluation at $\mathbf{x} = \mathbf{z}$, and n is the number of components. A common approach for determining if D is ever negative is to minimize D subject to the mole fractions summing to one. It is readily shown that the stationary points in this optimization problem can be found by solving the system of nonlinear equations:

$$\left[\left(\frac{\partial m}{\partial x_i} \right) - \left(\frac{\partial m}{\partial x_i} \right)_0 \right] - \left[\left(\frac{\partial m}{\partial x_n} \right) - \left(\frac{\partial m}{\partial x_n} \right)_0 \right] = 0 \quad \text{for } i = 1, 2, \dots, n-1 \quad (2)$$

$$1 - \sum_{i=1}^n x_i = 0 \quad (3)$$

If an Equation of State (EOS) model uses m , so that m is expressed in terms of \mathbf{x} and v , the molar volume of the mixture, then (2) and (3) must be solved simultaneously with the EOS. The model used here is the generalized cubic EOS

$$P - \frac{RT}{v-b} + \frac{a}{v^2 + ubv + wb^2} = 0 \quad (4)$$

The $(n+1) \times (n+1)$ system given by equations (2)-(4) above has a trivial root at $\mathbf{x} = \mathbf{z}$ and $v = v_0$ and frequently has multiple nontrivial roots as well. Thus conventional equation solving techniques such as Newton’s method may fail by converging to the trivial root or give an incorrect answer to the phase stability problem by converging to a stationary point that is not the global minimum of D .

Interval Newton/ Generalized Bisection Method

The Interval Newton/Generalized Bisection (IN/GB) algorithm can solve phase stability problems for a generalized cubic equation of state

model efficiently and with complete reliability. This Interval Newton/generalized bisection algorithm is entirely new method for solving these problems, a method that can guarantee with mathematical certainty that the correct solutions are found, thus eliminating computational problems that are frequently encountered with currently available techniques. The method is initialization independent; it is also model independent and can be applied in connection with other equations of state or with activity coefficient models.

Efficient techniques for implementing IN/GB are a relatively recent development, and thus such methods have not yet been widely applied. Schnepfer and Stadtherr have suggested the use of this method for solving chemical process modelling problems and can be successfully applied the method to chemical engineering problems.

Consider the solution of the system of real nonlinear equations $f(\mathbf{x}) = 0$, where it is desired to find all solutions in an specified initial interval $X(0)$. The basic iteration step in interval Newton methods is, given an interval $X(k)$, to solve the linear interval equation system

$$F'(X^{(k)})(N^{(k)} - x^{(k)}) = -f(x^{(k)}) \dots\dots\dots(5)$$

for a new interval $N^{(k)}$, where k is an iteration counter, $F'(X^{(k)})$ is an interval extension of the real Jacobian $f'(x)$ of $f(x)$ over the current interval $X^{(k)}$, and $x^{(k)}$ is a point in the interior of $X^{(k)}$, usually taken to be the midpoint. The interval extension $F\phi(X(k))$ of the Jacobian is determined by substituting the interval $X(k)$ for x in the expression $f'(x)$ for the real Jacobian, and performing interval operations in place of real operations. It can be shown that any root x^* of the set of equations that is within the current interval, i.e. $x^* \in X^{(k)}$, is also contained in the newly computed interval $N^{(k)}$. This suggests that the next iteration for X should be the intersection of $X(k)$ with $N(k)$, i.e. $X^{(k+1)} = X^{(k)} \cap N^{(k)}$. There are various interval Newton methods, which differ in how they determine $N^{(k)}$ from equation (5) and thus in the tightness with which $N^{(k)}$ encloses the solution set of (5).

NRTL Model

Interval Newton method is another approach for the phase stability analysis which was proposed about 10 years ago is a generalized bisection algorithm with some modifications and is relatively less sensitive to initial values, and provides all the roots including global optimum.

The activity coefficient model of NRTL predict multiple roots in phase equilibrium calculations. For

an n component system, the NRTL equation for the reduced molar excess Gibbs energy is as follows,

$$g^E(x) = \sum_{k=1}^n x_k \frac{\sum_{i=1}^n G_{ik} \tau_{ik} x_i}{\sum_{i=1}^n G_{ik} x_i}$$

where x_k is the mole fraction for species k, and G_{ik} and τ_{ik} are the NRTL binary interaction parameters. Above equation uses the mole fraction weighted averages of the interaction parameters to improve the efficiency of the interval method. The parameter G_{ik} is a function of τ_{ik} and the parameter $\tau_{ik} = a_{ik} \tau_{ik}$, and is given by

$$G_{ik} = \exp(a_{ik} \tau_{ik})$$

Statistical Associating Fluid Theory EOS Method

For a given mixture with or without multiple phases, the determination of phase stability is a key step in phase equilibrium computations, providing a global optimality test for the minimization of the total Gibbs energy. The determination of phase stability is typically done using tangent plane analysis. For a mixture at constant T, P, and composition (mole fractions) x_0 , the tangent plane condition is usually expressed in terms of the molar Gibbs energy of the mixture as a function of molar composition and volume (or density). The mixture is not stable if the molar Gibbs energy surface $g(X, \delta)$ ever falls below a plane tangent to the surface at x_0 .

The SAFT EOS is most conveniently expressed in terms of the Helmholtz energy. Here we use a “volume-based” formulation of tangent plane analysis in which the Helmholtz energy is the core function. For this case, the tangent plane condition is expressed in terms of the Helmholtz energy density (Helmholtz energy per unit volume of mixture) as a function of the molar component density vector $\rho = (\rho_1 \rho_2 \dots \rho_N)^T$. A mixture (the “feed” or “test phase”) at constant T, P and composition (molar densities) ρ_0 is not stable if the Helmholtz energy density surface $\alpha(\rho)$ ever falls below a plane tangent to the surface at ρ_0 .

The SAFT EOS is generally expressed in terms of the residual Helmholtz energy per unit mole of mixture α^{res} . There are hard sphere, dispersion, chain and association contributions that must be accounted for, so

$$\alpha^{res} = \alpha^{hs} + \alpha^{disp} + \alpha^{chain} + \alpha^{assoc} \quad (6)$$

Huang and Radosz described a model for SAFT. The hard sphere contribution α^{hs} is based on the hard sphere EOS as expressed by Boublik and is given by

$$\frac{\alpha^{hs}}{RT} = \frac{6}{\pi N_A \delta} \left[\frac{(\zeta_2)^3 + 3\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1 \zeta_2 (\zeta_3)^2}{\zeta_3 (1 - \zeta_3)^2} - \left(\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \right) \ln(1 - \zeta_3) \right] \quad (7)$$

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

Where δ is the total molar density of the mixture, x_i is the mole fraction of compound i in the mixture, N is the number of components in the mixture, N_A is Avogadro’s number, j is an exponent, and d_{ii} is the temperature-dependent segment diameter given by

$$d_{ii} = \sigma_i \left[1 - 0.12 \exp\left(\frac{-3u_i^0}{kT}\right) \right] \quad (4)$$

$$\text{Where } \sigma_i = \left(v_i^{00} \frac{6\tau}{\pi N_A} \right)^{1/3} \quad (5)$$

Where k is Boltzmann’s constant, and $\tau = \pi\sqrt{2}/6$ is the packing fraction for close-packed spheres. The dispersion term α^{disp} used by Huang and Radosz is

$$\frac{\alpha^{disp}}{RT} = m \sum_{i=1}^4 \sum_{j=1}^9 D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j \quad (6)$$

Where

$$m = \sum_{i=1}^N x_i m_i \quad (7)$$

$$\eta = \frac{\pi N_A \delta}{6} \sum_{i=1}^N x_i m_i d_{ii}^3 = \zeta^3 \quad (8)$$

$$\frac{u}{kT} = \frac{\sum_{i=1}^N \sum_{j=1}^N x_i x_j m_i m_j v_{ij}^0 \left(\frac{u_{ij}}{kT} \right)}{\sum_{i=1}^N \sum_{j=1}^N x_i x_j m_i m_j v_{ij}^0} \quad (9)$$

$$v_{ij}^0 = \left\{ \frac{1}{2} \left[(v_i^0)^{1/3} + (v_j^0)^{1/3} \right] \right\}^3 \quad (10)$$

$$u_{ij} = (1 - k_{ij}) (u_{ii} u_{jj})^{1/2} \quad (11)$$

$$v_i^0 = v_i^{00} \left[1 - 0.12 \exp\left(\frac{-3u_i^0}{kT}\right) \right]^3 \quad (12)$$

$$u_{ii} = u_i^0 \left(1 + \frac{e}{kT} \right) \quad (13)$$

The D_{ij} are the Chen and Kreglewski constants, $e/k = 10$,

The k_{ij} are binary interaction parameters

The chain term, α^{chain} by Chapman is based on the pair correlation function, $g_{ii}^{hs}(d_{ii})$ in the form of Boublik and is given by

$$\frac{\alpha^{chain}}{RT} = \sum_{i=1}^N x_i (1 - m_i) \ln(g_{ii}^{hs}(d_{ii})) \quad (14)$$

Where

$$g_{ii}^{hs}(d_{ii}) = \frac{1}{1-\zeta_3} + \frac{3d_{ii}}{2} \frac{\zeta_2}{(1-\zeta_3)^2} + 2 \left[\frac{d_{ii}}{2} \right]^2 \frac{(\zeta_2)^2}{(1-\zeta_3)^3} \quad (15)$$

The more general pair correlation function required is

$$g_{ii}^{hs}(d_{ii}) = \frac{1}{1-\zeta_3} + \frac{3d_{ii}d_{jj}}{d_{ii}+d_{jj}} \frac{\zeta_2}{(1-\zeta_3)^2} + 2 \left[\frac{d_{ii}d_{jj}}{d_{ii}+d_{jj}} \right]^2 \frac{(\zeta_2)^2}{(1-\zeta_3)^3} \quad (16)$$

The association term is α^{assoc}_i is

$$\frac{\alpha^{assoc}}{RT} = \sum_{i=1}^N x_i \left[\left\{ \sum_{A_i} [\ln X^{A_i} - \frac{X^{A_i}}{2}] \right\} + \frac{M_i}{2} \right] \quad (17)$$

where the summation over A_i indicates summation over all association sites on component i . Here M_i is

the number of association sites on component i , and X^{A_i} is the mole fraction of molecules of i which are not bonded at the association site A_i . This is determined from

$$X^{A_i} = [1 + N_A \sum_{j=1}^N \sum_{B_j} \rho_j X^{B_j} \Delta^{A_i B_j}]^{-1} \quad (18)$$

where the summation over B_j indicates summation over all association sites on component j .

When there are association effects to be accounted for, evaluation of the SAFT EOS requires an “internal” iteration to solve for the “internal” variables X^{A_i} , except in some special cases in which it is possible to solve for these variables explicitly. The strength function $\Delta^{A_i B_j}$ is defined as

$$\Delta^{A_i B_j} = g_{ii}^{hs}(d_{ii}) \left[\exp \left(\frac{A_i B_j}{kT} \right) - 1 \right] \sigma_{ij}^3 k^{A_i B_j} \quad (19)$$

Where $\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2}$ (20)

$\epsilon^{A_i B_j}$ and $k^{A_i B_j}$ are SAFT parameters.

Eqs. (1), (2), (6), (14) and (17) provide an expression for the SAFT EOS in terms of the molar residual

Helmholtz energy are (x, δ) given (at constant temperature) as a function of composition (mole fraction)

$x = (x_1, \dots, x_N)^T$ and total molar density δ .

Thus the SAFT EOS is most conveniently expressed in terms of the Helmholtz energy, as discussed above. Here a “volume-based” formulation of tangent plane analysis is used in which the Helmholtz energy is the core function and hence the tangent plane condition is expressed in terms of the Helmholtz energy density (Helmholtz energy per unit volume of mixture) as a

function of the molar component density vector $\rho = (\rho_1, \rho_2, \dots, \rho_N)^T$. A mixture (the “feed” or “test phase”) at constant T , P , and composition (molar densities) ρ_0 is not stable if the Helmholtz energy density surface $\alpha(\rho)$ ever falls below a plane tangent to the surface at ρ_0 .

CONCLUSION

In molecularly-based equations of state, SAFT approach have become increasingly popular tools for the modelling of phase behaviour. Using this, or even much simpler models, the reliable calculation of phase behaviour from a given model can be a very challenging computational problem. A new methodology is described that is the first completely reliable technique for computing phase stability and equilibrium from the SAFT model. The method is based on interval analysis, in particular an interval Newton/generalized bisection algorithm, which provides a mathematical and computational guarantee of reliability.

New techniques are presented that can also be exploited when conventional point-valued solution methods are used. These include the use of a volume-based problem formulation, in which the core thermodynamic function for phase equilibrium at constant temperature and pressure is the Helmholtz energy, and an approach for dealing with the internal iteration needed when there are association effects. This provides for direct, as opposed to iterative, determination of the derivatives of the internal variables.

An interval Newton/generalized bisection Algorithm is applied to problems modelled with cubic equations of state, and efforts were made to improve the computational efficiency of the approach, both for EOS models and for excess Gibbs energy models.

Systems which are non-ideal and the local composition model of NRTL may have multiple roots, the interval method successfully has predicts all the stationary points in the tangent plane distance function.

The SAFT EOS is most conveniently expressed in terms of the Helmholtz energy, we use a “volume-based” formulation of the phase stability and equilibrium problems at constant temperature and pressure, in which the core thermodynamic function is the Helmholtz energy.

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