

Lipschitz optimization for phase stability analysis: application to Soave–Redlich–Kwong equation of state

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Abstract

The Gibbs tangent plane analysis is the crucial method for the determination of the global phase stability and the true equilibrium compositions of the system at elevated pressures. Previous approaches have focused on finding stationary points of the tangent plane distance function (TPDF) described by the cubic equation of state. However, there is no complete guarantee of obtaining all stationary points due to the nonconvex and nonlinear nature of the models used to predict high pressure phase equilibria. After analyzing and reformulating the structure of the derivative function of the TPDF described by the Soave–Redlich–Kwong (SRK) equation of state, it was demonstrated that the Lipschitz constant of the TPDF can be obtained with the calculation precision satisfied. Then the phase stability problem can be solved with ε -global convergence. The calculation results for two examples state that the Lipschitz optimization algorithm, i.e., Piyavskii's univariate Lipschitz optimization algorithm used in this paper, can obtain the global minimum of the TPDF for binary mixtures at elevated pressures with complete reliability. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tangent plane analysis; High pressure phase equilibria; Lipschitz optimization; TPDF; Gibbs free energy

1. Introduction

The phase and chemical equilibrium calculation is of great importance in many chemical engineering applications, such as azeotropic distillation, supercritical extraction, three-phase distillation, petroleum and reservoir engineering. The ubiquity of the flash calculation in chemical engineering is just one example of its prevalence. Whereas robust algorithms are widely available for simple vapor–liquid equilibria, complications arise near phase boundary, when a vapor and two liquid phases are possible, in the vicinity of critical points, in the presence of chemical reactions [14]. So the

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determination of the phase stability, which is whether or not a given phase will split into multiphase, is a key step in phase equilibrium calculations. This is especially crucial for high pressure phase equilibria where even simple binary solution can exhibit complex phase behavior.

The phase stability problem is frequently formulated using the tangent plane criterion [1,12]. Recently, the global minimum of the tangent plane distance function (TPDF) was sought usually by solving a system of nonlinear equations for the stationary points [12,18]. Unfortunately, this computational method cannot find with complete certainty all the stationary points, even if no negative solutions are obtained for TPDF, the postulated configuration may still be unstable. Sun and Seider [17] applied a homotopy-continuation method in an attempt to locate all stationary points of the TPDF. However, no theoretical guarantee of identifying all stationary points of the TPDF can be given, as the formulation of the phase stability problem contains logarithmic terms. Hua et al. [5] presented an interval Newton method combined with a generalized bisection approach, which cannot present complete certainty, since this method ends up with intervals, it cannot be certain that within an interval there exist one or multiple solutions. Elhassan et al. [2] developed the original area method [3] into the case of N -components with two-phase system, and provided for the first time a rigorous mathematical proof that the equilibrium solutions satisfy the maximum area criterion, just as their own illustrations, their proof is necessary but not a sufficient condition for equilibrium. Zhu and Xu [20] extended the simulated annealing algorithm into the high pressure phase stability analysis on the basis of their successful prediction of liquid–liquid phase stability by above algorithm [19], however, the asymptotic convergence of the simulated annealing algorithm depends on the suitable choice of the ‘cooling schedules’, unsuitable ‘cooling schedules’ will lead to local solution for the phase stability problem. McDonald and Floudas [7–11] showed that for activity coefficient models, the problem could be reformulated to make it amenable to be solved by global optimization techniques: ε -global optimization method and branch and bound algorithm, which did mathematically guarantee that the correct answer was found for phase and chemical equilibrium problem. This is a true breakthrough in the liquid–liquid phase stability analysis and equilibrium calculation. But unfortunately, their transformations have not yet been identified for equations of state. Hence, the method is not yet applicable for multiphase equilibria in the retrograde region [14]. The high pressure phase equilibrium calculations, especially those close to the critical area, are highly dependent on the starting points, therefore, a reliable global optimization technique without worrying about the guess of the initiates is necessary and useful. In this paper, the Lipschitz optimization algorithm was used to obtain the global minimum of the TPDF described by Soave–Redlich–Kwong (SRK) equation of state. The calculation of the Lipschitz constant of the TPDF was solved by computing several linear programming and convex optimization problems. Two simple binary mixtures at high pressure was presented to check the global stability by a univariate Lipschitz optimization method, the results show that Lipschitz optimization can solve the phase stability problem with ε -global convergence.

2. The optimization formulation for phase stability analysis

Tangent plane analysis is crucial for the determination of the phase stability, whose derivation and figure illustrations were given by Baker et al. [1], and a first implementation was presented by Michelsen [12]. At specified temperature T , pressure P , and feed mole fraction z , a necessary and sufficient condition for a postulated solution to be an equilibrium one is that the TPDF, denoted by

$F(x)$, should be nonnegative for all possible phases in the system. The TPDF is defined as the distance between the Gibbs surface and the tangent plane associated with this surface at z . The component variables of the system are also subject to the normalized and nonnegative constrained conditions, therefore, the optimization formulation of the phase stability problem can be described as follows:

$$\min F(x) = g(x) - L(x) = \sum_{i=1}^N x_i \{ \mu_i(x) - \mu_i(z) \} \quad (1)$$

$$\text{s.t. } \sum_{i=1}^N x_i = 1 \quad (2)$$

$$0 \leq x_i \leq 1 \quad (3)$$

where $\mu_i(x)$ represents the chemical potential of component i at x , $\mu_i(z)$ represents the chemical potential of component i at z , $g(x)$ is the molar Gibbs free energy surface, and $L(x)$ is the tangent plane to the molar Gibbs free energy surface at z . If the tangent plane lies completely below the Gibbs surface, that means the TPDF $F(x)$ is nonnegative for all range of x , then the postulated solution corresponds to a global minimum of the Gibbs free energy. If not, a phase equilibrium calculation with lower Gibbs free energy must be found in another procedure.

3. Lipschitz optimization

Lipschitz optimization was first proposed by Piyavskii (pp. 413–421 in Ref. [4]) and Shubert [15], respectively, for one-dimensional intervals. An extension to the n -dimensional case was proposed by Maldineo [6]. The general Lipschitz algorithms without or with constrained conditions, and their global convergence proofs were illustrated thoroughly by Horst and Pardalos [4]. A real-valued function f is called Lipschitz function on a set $M \subset R^n$ if there is a constant $L = L(f, M) > 0$ such that:

$$|f(x) - f(y)| \leq L \|x - y\| \quad \forall x, y \in M \quad (4)$$

where $\|\cdot\|$ denotes the Euclidean norm. It is well known that all continuously differentiable functions f with bounded gradients on M are Lipschitz function on M , where:

$$L = \sup\{\|\nabla f(x)\| : x \in M\} \quad (5)$$

is a Lipschitz constant. Obviously, if f is a Lipschitz function with constant L , then f is also Lipschitz function with all constants $L' > L$.

Note that the following general approach for solving the nonconvex optimization problem:

$$\min f(x) \quad \text{s.t. } x \in M \quad (6)$$

with $M \subset R^n$ nonempty and compact and f is a Lipschitz function on M . Start with an arbitrary point $x^0 \in D$, define the first underestimation function by:

$$F_0(x) = f(x^0) - L\|x - x^0\| \quad (7)$$

and the next iteration point by:

$$x^1 = \arg \min F_0(x). \quad (8)$$

In step k , the underestimation function is:

$$F_k(x) = \max_{0 \leq i \leq k} \{f(x^i) - L\|x - x^0\|\} \quad (9)$$

and the next iteration point is:

$$x^{k+1} = \arg \min F_k(x). \quad (10)$$

The stop criterion for Lipschitz optimization is that the difference between the original function value and the underestimation function value is lower than the specified global tolerance ε .

4. Calculation of the Lipschitz constant for the tangent plane distance function modeled by SRK equation of state

SRK equation of state is used to describe the TPDF for the mixture at elevated pressures [16]. For the mixture at constant temperature T and pressure P , it is presented as:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \quad (11)$$

where v is the molar volume of the mixture, and a and b are the equation parameters for the whole mixture, calculated according to the following mixing rule:

$$a = \sum_{i=1}^N \sum_{j=1}^N x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \quad (12)$$

$$b = \sum_{i=1}^N x_i b_i \quad (13)$$

where x_i is the mole fraction of the component i in the mixture, k_{ij} is the interaction parameter between component i and component j , and a_i and b_i are the SRK parameters of the pure component i in the mixture which are calculated by follows:

$$a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \left[1 + (0.480 + 1.574 \omega_i - 0.176 \omega_i^2) (1 - T/T_{ci}^{0.5}) \right]^2 \quad (14)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (15)$$

where R is the gas constant, T_{ci} and P_{ci} are the critical temperature and pressure of the component i , ω_i is the acentric factor of the component i . In the mixture, the fugacity coefficient of component i is calculated by:

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln Z + \ln \frac{v}{v - b} + \frac{a}{bRT} \left[\frac{b_i}{b} - \frac{2}{a} \sum_{j=1}^N x_j (a_i a_j)^{1/2} (1 - k_{ij}) \right] \ln \frac{v + b}{v}. \quad (16)$$

There are only $N - 1$ independent variables in Eq. (1) according to the constrained condition described by Eq. (2). Then, TPDF $F(x)$ can be expressed on the basis of the front $N - 1$ component variables in the mixture, then:

$$F(x) = \sum_{i=1}^{N-1} x_i \{ \mu_i(x) - \mu_i(z) \} + \left(1 - \sum_{i=1}^{N-1} x_i \right) \{ \mu_N(x) - \mu_N(z) \} \quad (17)$$

where $\mu_N(x)$ and $\mu_N(z)$ are the chemical potentials of the component N at x and z , respectively. The i -th derivative function of the TPDF can be obtained by derivation above function by the i -th component variable, x_i , with other component variables keeping constant:

$$F'_i(x) = \mu_i(x) - \mu_i(z) - \mu_N(x) + \mu_N(z) + \sum_{j=1}^N x_j \mu'_j \quad i = 1, 2, \dots, N - 1. \quad (18)$$

According to the Gibbs–Duhem equation of the chemical potential function at constant temperature and pressure, the following equation is satisfied:

$$\sum_{j=1}^N x_j \mu'_j = 0 \quad (19)$$

so, Eq. (18) can be written as

$$F'_i(x) = \mu_i(x) - \mu_i(z) - \mu_N(x) + \mu_N(z) \quad i = 1, 2, \dots, N - 1. \quad (20)$$

Substituting the fugacity coefficient definitions of the chemical potentials for the component i and N into Eq. (20), the i -th derivative function of the TPDF becomes:

$$\begin{aligned} F'_i(x) &= \ln \phi_i x_i - \ln \phi_N x_N - \mu_i(z) + \mu_N(z) \\ &= \ln \phi_i - \ln \phi_N + \ln x_i - \ln x_N - \mu_i(z) + \mu_N(z) \quad i = 1, 2, \dots, N - 1. \end{aligned} \quad (21)$$

Substituting Eq. (16) into Eq. (21), the following equation can be obtained by some rearrangements:

$$\begin{aligned} F'_i(x) &= \frac{b_i}{b} Z + \frac{b_N}{b} + \frac{ab_i}{b^2 RT} \ln \frac{v+b}{v} - \frac{b_N}{b} Z - \frac{b_i}{b} - \frac{ab_N}{b^2 RT} \ln \frac{v+b}{v} \\ &\quad - \frac{2}{bRT} \left\{ \sum_{j=1}^N x_j \left[(a_i a_j)^{1/2} (1 - k_{ij}) - (a_N - a_j)^{1/2} (1 - k_{Nj}) \right] \right\} \ln \frac{v+b}{v} \\ &\quad + \ln x_i - \ln x_N - \mu_i(z) + \mu_N(z) \quad i = 1, 2, \dots, N - 1. \end{aligned} \quad (22)$$

At constant temperature and pressure, the SRK parameters of the mixture, a and b , are of composition-dependence. $a(x)$ is a convex function, and $b(x)$ is a linear function according to Eqs. (12) and (13) in the composition space. So $a(x)$ and $b(x)$ are bounded in the feasible region described by Eqs. (2) and (3). Their upper and lower bounds can be obtained by convex optimization or linear programming modeled as follows: min or max is Eq. (12), s.t. Eqs. (2) and (3), and min or max is Eq. (13), s.t. Eqs. (2) and (3), respectively.

The bounds of the molar volume of the mixture, v , is determined by the following equations obtained according to Eq. (11):

$$v = b + RT / (p + a/v(v+b)) > b, \quad (23)$$

$$v = b + RT / (p + a/v(v+b)) < b + RT/p. \quad (24)$$

Then, the molar volume, v , lies in the range of $b - RT/P + b$. Consequently, the compressibility factor Z lies in the range of $pb/RT - 1 + pb/RT$. The upper and lower bounds of the first six terms in Eq. (22) can be calculated by substituting the upper or lower bounds of the a , b , v or Z into each term. The seventh term in Eq. (22) is also bounded, because the following linear function, $L^U(x)$, is also bounded, and its upper and lower bounds can be obtained by the following linear programming: min or max is:

$$L^U(x) = \sum_{j=1}^N x_j \left[(a_i a_j)^{1/2} (1 - k_{ij}) - (a_N a_j)^{1/2} (1 - k_{Nj}) \right] \quad (25)$$

and s.t. Eqs. (2) and (3).

Substituting the upper or lower bounds of a , b , v or $L^U(x)$ into the seventh item of Eq. (22), its upper and lower bounds can be calculated. The function $\ln x$ is a monotone increasing function, its lower and upper bounds occur at $-\alpha$ and 0.0 when x is equals to 0.0 and 1.0, respectively. Then, the value of $\ln x_i$ or $\ln x_N$ does not exist when x_i or x_N are equal to zero, this states that the derivative function of the TPDF is not continuous at zero point. Here, a very small positive real number, such as $\delta = 10^{-7}$, can be used to construct a feasible calculation interval $[\delta, 1 - \delta]$ for variables x_i and x_N . Therefore, the upper and lower bounds of $F'_i(x)$ can be obtained with the calculation precision satisfied. The bound with the larger absolute value is taken as the minimal

Initialization

$$\begin{aligned} k &= 1; \\ x_1 &= \frac{a+b}{2}; \\ x_{opt} &= x_1; \\ f_{opt} &= f(x_{opt}); \\ F_{opt} &= f_{opt} + \frac{L(b-a)}{2}; \\ F_1(x) &= f(x_1) + L|x - x_1|; \end{aligned}$$

Piyavskii's saw-tooth cover

$$\begin{aligned} \text{While } F_{opt} - f_{opt} > \varepsilon \quad \text{do} \\ x_{k+1} &= \arg \min_{x \in [a,b]} F_k(x); \\ \text{if } f(x_{k+1}) > f_{opt} \quad \text{then } f_{opt} &= f(x_{k+1}); \quad x_{opt} = x_{k+1} \quad \text{endif}; \\ F_{k+1}(x) &= \max_{i=1,2,\dots,k+1} \{f(x_i) + L|x - x_i|\}; \\ F_{opt} &= \min_{x \in [a,b]} F_{k+1}(x); \end{aligned}$$

EndWhile.

Fig. 1. The calculation scheme of Piyavskii algorithm.

Table 1

The maximal and minimal values of a , b , v and Z in composition space for system 1

Parameters	a (Pa m ³ K ^{1/2} /mol)	b (m ³ /mol)	v (m ³ /mol)	Z
max	0.57293	2.70×10^{-5}	41.7×10^{-5}	1.069
min	0.21425	2.68×10^{-5}	2.68×10^{-5}	0.069

Lipschitz constant. If there are only two components in the mixture, Eq. (22) is an univariate function, and can be written as:

$$\begin{aligned}
 F'_i(x) = & \frac{b_1}{b}Z + \frac{b_2}{b} + \frac{ab_1}{b^2RT} \ln \frac{v+b}{v} - \frac{b_2}{b}Z - \frac{b_1}{b} \\
 & - \frac{ab_2}{b^2RT} \ln \frac{v+b}{v} - (2x_i - 1) \frac{2}{bRT} \ln \frac{v+b}{v} (a_1 a_2)^{1/2} (1 - k_{12}) \\
 & + \ln x_1 - \ln x_2 - \mu_1(z) + \mu_2(z).
 \end{aligned} \quad (26)$$

Its upper and lower bounds can be calculated according to above methods described, one specific example is presented in Example 1.

5. Calculation results and discussion

Two binary mixtures at high pressures with different charges were used to predict the phase stability by one simple univariate Lipschitz optimization algorithm, i.e., Piyavskii's algorithm (p. 414 in Ref. [4]) presented in Fig. 1. The Lipschitz constant of the TPDF is taken as 40.0 for Example 1 on the basis of upper and lower bound estimations of its derivative function, and 50.0 for Example 2. The convergence tolerance, ε , is taken as 10^{-5} in this paper. All computations were performed on a SGI IRIS Indigo workstation with CPU 100 MHz, and all CPU seconds reported represent the real time

Table 2

The maximal and minimal values of each term in Eq. (26) for Example 1 with the overall composition $z = \{0.5, 0.5\}$

Item	max	min
$(b_1/b)Z$	1.0809	0.0690
b_2/b	1.0	0.9926
$(ab_1/b^2RT) \ln(v+b/v)$	9.50	0.3340
$-(b_2/b)Z$	-0.9926	-1.0690
$-(b_1/b)$	-1.0	-1.0112
$-(ab_2/b^2RT) \ln(v+b/v)$	-0.3317	-9.43
$(2x-1)(a_1 a_2)^{1/2}(1-k_{12})(2/bRT) \ln(v+b/v)$	10.61	-10.61
$\ln x$	0	-16.12
$-\ln(1-x)$	16.12	0
$-\mu_1^0(z)$	-0.01377	-0.01377
$-\mu_2^0(z)$	1.5004	1.5004
Total	37.474	-35.359

Table 3

Phase stability analysis results for Example 1 by Lipschitz optimization

Hydrogen sulfide (1)–methane (2) at 190.0 K and 40.53 bar

Component	x_i	x_i^{\min}	F^{\min}	Iteration	CPU (s)
1	0.50	0.07457			
2	0.50	0.92543	−0.08240	24 355	181.58
1	0.0187	0.07669			
2	0.9813	0.92331	−0.00397	24 983	193.78
1	0.8880	0.07926			
2	0.1120	0.92704	−0.00213	26 643	223.66

taken to solve the phase stability problem by the Piyavskii's algorithm. It should be noted that Piyavskii (p. 415 in Ref. [4]) mentioned that the number of subproblems might become very large and that scanning their list to find the subproblem with the smallest lower bound was time consuming. However, this problem, as well as that of subproblem elimination, can be done much efficiently with an adequate data structure, i.e., a double-ended priority queue. It can be efficiently realized through min–max heaps. In the following tables, when the value does not exceed 10^{-7} , in double precision, an entry of zero was recorded.

5.1. Example 1: hydrogen sulfide (1) + methane (2)

This is a binary mixture with up to two phases at 190 K and 40.53 bar. The SRK equation of state was used with parameters calculated from $T_{c1} = 373.2$ K, $P_{c1} = 89.4$ bar, $\omega_1 = 0.1$, $T_{c2} = 190.6$ K, $P_{c2} = 46.0$ bar, $\omega_2 = 0.008$, and a binary interaction parameters $k_{12} = 0.08$. This system was studied by Hua et al. [5], Michelsen [12], and Sun and Seider [17] as a typical example. For feed composition $z = \{0.5, 0.5\}$, there are multiple stationary points in its TPDF drawn by Sun and Seider [17]. The upper and lower bounds of parameters, i.e., a , b , v and Z , in Eq. (26) are supplied in Table 1. The maximal and minimal values of each term in Eq. (26) are calculated and supplied in Table 2. Obviously, the value 40.0 used in this paper is also a Lipschitz constant for the TPDF at $z = \{0.5, 0.5\}$. The postulated one-phase is unstable because the global minimum of its TPDF described in Table 3, −0.08240, was converged at $\{0.07457, 0.92543\}$ by Piyavskii's algorithm. For another two

Table 4

Phase stability analysis results for Example 2 by Lipschitz optimization

Methane (1)–propane (2) at 277.6 K and 100 bar

Component	x_i	x_i^{\min}	F^{\min}	Iteration	CPU (s)
1	0.68	0.77160			
2	0.32	0.22840	−0.00029	94 127	329.02
1	0.73	0.64898			
2	0.27	0.35102	-3.34×10^{-4}	107 533	375.88
1	0.40	0.40			
2	0.60	0.60	0.0	37 899	132.47

overall compositions, $\{0.0187, 0.9813\}$ and $\{0.88, 0.112\}$, their global minima were also obtained and given in Table 3, the negative global minima of their TPDF state that they are all unstable for one postulated phase. Our calculation results are consistent with those given by Hua et al. [5] and Sun and Seider [17].

5.2. Example 2: methane (1) + propane (2)

This is a binary mixture of methane and propane at a temperature of 277.6 K and a pressure of 100 bar. The SRK equation of state was used with parameters calculated from the methane pure component properties given above, and $T_{c2} = 369.8$ K, $P_{c2} = 42.5$ bar, $\omega_2 = 0.152$, and a binary interaction parameters $k_{12} = 0.029$. Three different overall compositions described in Table 4 were used to check the global phase stability by the univariate Lipschitz optimization algorithm. The former two overall compositions, $\{0.68, 0.32\}$ and $\{0.73, 0.27\}$, are unstable because the global minima of their TPDF are negative. The last overall composition, $\{0.4, 0.6\}$, is stable for one postulated phase at above temperature and pressure. Our results are consistent with those given by Hua et al. [5] and Prausnitz et al. [13].

6. Conclusion

In this paper, the Lipschitz optimization was applied for the high pressure phase stability analysis problem modeled by cubic equation of state. The calculation of Lipschitz constant for the TPDF modeled by SRK equation of state was obtained by the upper and lower bounds of the parameters, which were obtained by optimizing several convex or linear functions in the feasible composition space. The phase stability problem can be solved by Lipschitz optimization techniques with ε -global convergence. The calculation results for two binary mixtures state that the Lipschitz optimization algorithm, i.e., Piyavskii's univariate Lipschitz optimization algorithm, can obtain the global minimum of the TPDF at elevated pressure with complete reliability. It should be noted that Eq. (22) in this paper is obtained for N -component case, then the stability analysis of the systems containing three or more species can be solved by multivariate Lipschitz optimization algorithms.

7. List of symbols

Notations

a	Parameter of SRK equation of state
b	Parameter of SRK equation of state
v	Molar volume
Z	Compressibility factor
L	Lipschitz constant
N	The number of components
z_i	Feed molar composition of component i
$F(x)$	Tangent plane distance
g	Molar Gibbs free energy

min	Minimum
max	Maximum
sup	Supremum
$F_k(x)$	Underestimating function
P	Pressure (atm or bar)
T	Temperature (K)
T_c	Critical temperature (K)
P_c	Critical pressure (bar)
ω	Acentric factor
x_i	Mole fraction of component i
k	Binary interaction parameters for SRK or PR

Greek symbols

$\mu_i(z)$	Chemical potential of component i at z
$\mu_i(x)$	Chemical potential of component i at x
ϕ_i	Fugacity coefficient

Acronyms

TPDF	Tangent plane distance function
s.t.	Subject to

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