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Efficient location of multiple global minima for the phase stability problem

Dan Vladimir Nichita [a,b,*], Susana Gomez [c]

[a] CNRS UMR 5150, Laboratoire des Fluides Complexes, Université de Pau et des Pays de l'Adour, B.P. 1155, 64013 Pau Cedex, France
[b] Instituto Mexicano del Petroleo, Programa de Yacimientos Naturalmente Fracturados, Eje Central Lazaro Cardenas 152, Delegacion G.A. Madero, 07730 Mexico D.F., Mexico
[c] Instituto de Investigacion en Matematicas Aplicadas y Systemas, Universidad Nacional Autonoma de Mexico, Apdo. Postal 20-726, Delegacion Alvaro Obregon, 01000 Mexico D.F., Mexico

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ABSTRACT

Phase stability testing is an important subproblem in phase equilibrium calculations. Phase stability analysis consists in finding either all stationary points or only the global minimum of the tangent plane distance (TPD) function. The TPD surface is non-convex and may be highly non-linear, and many phase stability calculations are rather difficult. In this work we are solving the phase stability problem using the tunneling global optimization method and a modified objective function; all stationary points of the TPD function are global minima of this objective function. For finding all its global minima at the same level (known, with objective function equal to zero), we exploit a unique feature of the tunneling method, which is able to find efficiently and reliably multiple minima at the same level. Numerical experiments for various difficult phase equilibrium problems show that the tunneling method is a powerful and reliable tool for global phase stability testing.

1. Introduction

Phase stability analysis is a key step in phase equilibrium calculations. It provides the correct answer on whether or not a feed is thermodynamically stable at given conditions. It can be used for phase assignment (vapor or liquid), for initializing a phase split, and for validating the results of flash calculations (i.e. the phase repartition corresponds to the global minimum of Gibbs free energy). The phase stability criteria first set by Gibbs [1] were clearly presented and discussed by Baker et al. [2] and Michelsen [3]. The most frequent formulation of the phase stability problem is in terms of Michelsen's TPD function and the problem is solved either by directly minimizing the TPD function or by solving an equivalent non-linear system of equations.

The difficulty of phase equilibrium calculations consists in the highly non-linear and non-convex form of the objective function that gives no guarantee that the global minimum will be found. The complexity of the problem increases near critical points and phase boundaries. Local methods may be very fast, but they are finding a single stationary point for a given initial guess, which can be a local minimum or a saddle point. Even global methods do not all guarantee that the global minimum is found, and they are generally expensive, the computation cost being sometimes unaffordable, even for moderate problems. For solving the phase stability problem, several global optimization methods have been used: Newton-Interval [4,5], homotopy continuation [6], branch and bound [7,8], simulated annealing [9,10], and tunneling [11–17]. Wasylkiewicz et al. [18] track ridges and valleys of the TPD function to find its stationary points. The dividing rectangles method used by Saber and Shaw seems to be highly efficient for solving phase stability [19]. Some (few) of these methods are looking for all stationary points, while others give only the global minimum of the TPD function.

Balogh et al. [20] have recently successfully used a modified objective function [21] (see also [22,23]) for phase stability analysis, and a stochastic method based on a space search, that does not need gradient evaluations. The modified objective function has the particularity that multiple global minima are at the same level (known, with the value of the objective function equal to zero).

In this work we adopt the same modified objective function for phase stability, but we use the tunneling global optimization (gradient-based) method, which has a feature that recommends it particularly for this specific problem: the ability of reliably and efficiently finding multiple minima at the same level. For instance, all the 18 global minima at the same level of the Schubert function (which even for $n = 2$ exhibits a highly complex landscape with

* Corresponding author at: CNRS UMR 5150, Laboratoire des Fluides Complexes, Université de Pau et des Pays de l'Adour, B.P. 1155, 64013 Pau Cedex, France. Tel.: +33 5 5940 7699; fax: +33 5 5940 7725.
E-mail addresses: dnichita@univ-pau.fr, dvnichita@hotmail.com (D.V. Nichita).

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Nomenclature

D	tangent plane distance function
$\tilde{D}$	dimensionless tangent plane distance function
f	objective function
f_i	fugacity of component i
k_i	given by Eq. (4)
k^*	values of k at stationary points
k_{ij}	binary interaction parameter between components i and j
n	number of independent variables
nc	number of components
$nlev$	maximum number of global minima searched by the code
p	pressure
R	universal gas constant
T	temperature
$T(x)$	tunneling function
$T_c(x)$	classical tunneling function
$T_e(x)$	exponential tunneling function
x_i	mole fraction of component i in the trial phase
x	independent variable (Section 3)
x_m	stationary points
x_{tu}	feasible point in another valley of the objective function
Z	compressibility factor
z_i	feed composition

Greek letters

δ_{ij}	the Kronecker delta
φ_i	fugacity coefficient of component i
λ_m	strength of the pole at the point x_m
Φ	modified objective function

Subscript

i,j	component index

Superscripts

T	transposed
$*$	at stationary points

760 local minima) have been successfully found with the tunneling method [24]. The cubic equations of state (EoS) we use here are the Soave–Redlich–Kwong (SRK) EoS [25], and the Peng–Robinson (PR) EoS [26]. The tunneling method is tested for several difficult problems involving mixtures from binary to quaternary.

In our previous work on phase stability with tunneling, only the global minimum of the TPD function was searched; the entire philosophy behind this paper is different: in this paper we find (i) all stationary points of the objective function, (ii) using a feature of the tunneling global optimization method not used before in phase stability calculations, and (iii) using a modified objective function which is highly appropriate for exploiting this particular ability of the tunneling method. Knowledge of all stationary points is important from both theoretical and practical points of view; towards the end of the manuscript, we discuss the potential use of all known stationary points in initializing multiphase equilibrium calculations.

The paper is structured as follows: we first present the modified objective function used in this work, then we describe the tunneling global optimization method, with emphasis to its ability to find multiple minima at the same level; results are presented for various difficult numerical experiments, before resuming a discussion and the concluding remarks.

2. The modified TPD function

The dimensionless TPD function, Michelsen [3], has the form

$$\tilde{D}(\boldsymbol{x}) = \frac{D(\boldsymbol{x})}{RT} = \sum_{i=1}^{nc} x_i(\ln f_i(\boldsymbol{x}) - \ln f_i(\boldsymbol{z})) \tag{1}$$

where $\boldsymbol{z} = (z_1, \ldots, z_{nc})^T$ is the feed composition and $\boldsymbol{x}$ is the trial phase composition. The vector of primary variables is $\boldsymbol{x} = (x_2, \ldots, x_{nc})^T$; here we have considered the mole fraction of component 1 as dependent variable

$$x_1 = 1 - \sum_{i=2}^{nc} x_i \tag{2}$$

The minimization problem is

$$\begin{array}{ll} \text{Find} & \min \tilde{D}(x) \\ \text{s.t.} & 0 \le x_i \le 1; \quad i = 2, nc \end{array}$$

The TPD function can be written as

$$\tilde{D}(\boldsymbol{x}) = \sum_{i=1}^{nc} x_i k_i(\boldsymbol{x}) \tag{3}$$

where

$$k_i(\boldsymbol{x}) = \ln \varphi_i(\boldsymbol{x}) + \ln x_i - h_i(\boldsymbol{z}); \quad i = 1, nc \tag{4}$$

and

$$h_i(\boldsymbol{z}) = \ln \varphi_i(\boldsymbol{z}) + \ln z_i; \quad i = 1, nc \tag{5}$$

In this work we use the modified objective function for phase stability analysis [21]:

$$\Phi(\boldsymbol{x}) = \sum_{i=1}^{nc} [k_{i+1}(\boldsymbol{x}) - k_i(\boldsymbol{x})]^2 \tag{6}$$

where for convenience $k_{nc+1}(\boldsymbol{x}) = k_1(\boldsymbol{x})$.

The modified minimization problem is

$$\begin{array}{ll} \text{Find} & \min \Phi(x) \\ \text{s.t.} & 0 \le x_i \le 1; \quad i = 2, nc \end{array}$$

The minimum value of the objective function is $\Phi(\boldsymbol{x}^*) = 0$, where $\boldsymbol{x} = \boldsymbol{x}^*$ are n_s stationary points of Φ, for

$$k_1(\boldsymbol{x}^*) = k_2(\boldsymbol{x}^*) = \cdots = k_{nc}(\boldsymbol{x}^*) = k^* \tag{7}$$

From Eq. (4), for each minimizer $\boldsymbol{x}^*$ we have

$$k_i^* = k_i(\boldsymbol{x}^*) = \ln \varphi_i(\boldsymbol{x}^*) + \ln x_i^* - h_i(\boldsymbol{z}); \quad i = 1, nc \tag{8}$$

Geometrically, k^* [21] is the distance between two hyperplanes tangent to the Gibbs energy surface and parallel to the hyperplane tangent at $\boldsymbol{z}$. The zeros of the modified objective function occur for the same mole fractions $\boldsymbol{x}$ as the stationary points of the TPD function, and k^* is equal to $\tilde{D}$ (as it follows Eq. (8)).

A mixture is stable at given pressure, temperature and composition if *all* $k^* \ge 0$; a negative value of k^* indicates an unstable feed which split into two or more stable phases. To establish the phase status for a given feed one must find *all* the global minima at the same level ($\Phi = 0$). Finding all zeros of Φ is definitely not an easy task. The tunneling gradient-based global optimization method has an extremely attractive feature that can be used to solve this particular problem: its ability to efficiently and reliably find all multiple minima at the same level.

To apply a gradient-based optimization method one needs the elements of the gradient vector

$$g_j = \frac{\partial \Phi}{\partial x_j} = 2\sum_{i=1}^{nc}(k_{i+1} - k_i)\left(\frac{\partial k_{i+1}}{\partial x_j} - \frac{\partial k_i}{\partial x_j}\right); \quad j = 2, nc \tag{9}$$

where

$$\frac{\partial k_i(\boldsymbol{x})}{\partial x_j} = \frac{\partial \ln f_i(\boldsymbol{x})}{\partial x_j} - \frac{\partial \ln f_i(\boldsymbol{x})}{\partial x_1}; \quad i = 1, nc; \; j = 2, nc \tag{10}$$

and

$$\frac{\partial \ln f_i(\boldsymbol{x})}{\partial x_j} = \frac{\delta_{ij}}{x_i} + \frac{\partial \ln \varphi_i(\boldsymbol{x})}{\partial x_j}; \quad i, j = 1, nc \tag{11}$$

Here the partial derivatives of fugacity coefficients with respect to mole fractions are evaluated analytically. For cubic EoS this is a simple task (and derivatives can be coded quite efficiently [27]), but for more complex, non-cubic EoS this could be rather difficult, and numerical derivatives must be used. Automatic differentiation could be an alternative option.

3. The tunneling global optimization method

The tunneling methods [28–31] are deterministic methods in the sense that they find a sequence of local minima with a monotonically decreasing value of the objective function. They have a minimization phase where starting from an initial point x_0, a local minimum x^* is found with $f^* = f(x^*)$, and then the method *tunnels* (in the tunnelization phase) to another valley of the objective function, which means finding a feasible point x^{tun}, with $f(x^{tun}) \leq f^*$ (the reader can find an illustration of the basic principles of the tunneling method in Figs. 1 and 2 from Ref. [15]). This point will be taken as the initial point x_0 for the next minimization phase and these two phases are repeated alternatively until convergence to the global solution is achieved. These methods have the following properties: they find a sequence of local minima with decreasing function values $f(x_1^*) \geq f(x_2^*) \geq \cdots \geq f(x_G^*)$, ignoring all the local minima with larger objective function than the best already found; as in any other method they can find minima at the same level and never find again the same minimum. For both phases, minimization and tunnelization, the same local optimization descent method can be used. The gradient-based local bounded method used by the code used in this work is a limited memory quasi-Newton method, L-BFGS-B [32,33]. In the BFGS method the Hessian is approximated based on the information from previous iterations, and the method converges with a supralinear rate. An exact Hessian (full Newton approach) gives a second order convergence, but has a smaller, in some cases much smaller, convergence radius. Note that BFGS always converges starting from the standard initialization of phase stability, while a full Newton method is usually not converging starting from the same initial guess, sculptured initialization or a number of iterations of some other methods (like for instance successive substitution) are required.

The step generated by the bound constrained optimization local method (used in both minimization and tunneling phases) is designed to force the new iterate to be within the bounds. When a descent direction has been created, a Cauchy step is performed to see which independent variables reach their bounds and thus will remain fixed during this step; at this level the linear constraint (Eq. (2)) is also checked to decide if the variables can be moved along the descent direction. After that, a linear search is performed to find the step-length on the free variables, and if the variables of the linear constraint were free, the step-length will take into consideration the linear constraint again, to ensure that the step is taken preserving the constraint satisfaction, which ensures that the dependent variable (x_1) is positive.

The tunneling methods also have a stochastic element as they take the initial point to start the search for points in another valley (tunnelization phase) in random directions within a neighbourhood of the last local minimum. It is this stochastic element that can be exploited to perform a smart exploration of the feasible space and a parallelization, see [34]. A detailed description of the sequential methods can be found in Levy and Montalvo [29] and Barron and Gomez [31]. Here we give only a brief description.

Once a local minimum has been obtained using any local method, to be able to tunnel from one valley to another using gradient-type methods, it is necessary to *destroy* the minimum, placing a pole at the minimum point x^* and generating directions that would move the iterates away from it. To find a point x^{tun} in another valley with a value less than or equal to $f(x^*)$, one has to solve the following inequality:

$$T(x) = f(x) - f(x^*) \leq 0 \tag{12}$$

and in order to be able to move away from the local minimum, using gradient information, it is necessary to destroy the minimum by placing a pole at x^* using any of the *tunneling functions*, either the exponential tunneling function [31]

$$T_e(x) = (f(x) - f^*)\exp\left(\frac{\lambda^*}{||x - x^*||}\right) \tag{13}$$

or the classical tunneling function [30]

$$T_c(x) = \frac{f(x) - f^*}{||x - x^*||^{\lambda^*}} \tag{14}$$

Solving problem (12) now consists in finding x^{tun} such that

$$T_e(x^{tun}) \leq 0 \quad \text{or} \quad T_c(x^{tun}) \leq 0 \tag{15}$$

We can take descent directions to solve this inequality problem, and thus we use the same algorithm used to find the local minimum with appropriate stopping conditions to check convergence for problem (15).

3.1. Minima at the same level

There are very few methods with the capability to find several minima at the same level, that is with the same value of the objective function, $f(x_1^*) = f(x_2^*) = \cdots = f(x_t^*)$, without finding again the minimum already found.

Although in principle several methods should be able to find these minima, like branch and bound and interval methods, in practice the computational cost makes them unaffordable. Stochastic methods like evolutionary methods cannot guarantee that the same minimum is not found again, and thus even in the case when the global level (lower bound) of the function is known, these methods can never guarantee finite convergence.

One of the most attractive characteristics of the tunneling methods is the fact that they can find minima at the same level in the tunneling phase, as in this phase one looks for a point x_{tu} in another valley where $f(x_{tu}) \leq f^*$, and the equality implies a point at the same level $f(x_{tu}) = f^*$. Actually, the local optimization method just checks in the minimization phase that these points are indeed minima or simply will iterate to get the desired precision (this will appear in the tables reporting the solution of our numerical examples). Also, in order to avoid going back to minima already found (that would satisfy the equality again), it is necessary to keep "turned-on" the poles used to destroy the minima found before, and the tunneling function now becomes

$$T(x) = (f(x) - f^*)\prod_{i=1}^{t}\exp\left(\frac{\lambda_i^*}{||x - x_i^*||}\right) \tag{16}$$

As it could happen that the method encounters several minima (say t) at the same level before it finds the global level, as soon as a minimum at a lower level is found, t is set to 1, as the history of these minima will no longer be needed, because the method will never find again a point with higher value of the objective function (it always decreases).

The tunneling method has successfully been used for solving problems with multiple minima at the same level; for instance the Schubert problem with $n = 2$ has 18 global minima which have been correctly and efficiently found [24]. Actually, this is the first time that results on real applications with this feature are being reported.

3.2. Starting points for the tunneling phase

Another key aspect of these methods is how to take the initial point from which the tunneling search starts. First, and for a pre-fixed number of points, the search will start from points x in a neighbourhood of the last (and best) local minimum found, and will be taken along random directions, $x = x^* + er$, where e is a scalar that defines the neighbourhood and depends on the scale of the problem, and r is a random vector within $[-1, 1]$. From these initial points the tunneling search starts looking for a point in another valley, solving inequality (15). If the search from this set of neighbouring points is not successful, another pre-fixed number of random points are then taken anywhere at the feasible region.

The stochastic element in the tunneling phase is related to the initial point of this phase; this initial point is selected in a random direction from the last local minima found, in a neighbourhood that depends on the scale of the problem. Then, the number of function and gradient evaluations may vary, if the random direction changes, but the method will locate all global minima, if sufficient computing time is allowed (i.e. a large enough number of initial points in the tunneling phase). The maximum number of initial points allowed for the tunneling phase serves also to control the amount of computing effort designed to check for global optimality. In this paper, we have used the default option of max $(20, 5n)$ initial points. This default option is chosen on the basis of author's previous experience in solving a variety of optimization problems, quite different in nature, from pure theoretical highly difficult benchmark problems to large practical problems in petroleum and chemical engineering.

3.3. Precision details

The robustness of the method depends strongly on the proper selection of the different tolerances and of their relative value. Here, we will describe the most important tolerances related to our application problem.

The stopping condition for a successful tunneling, that is $T(x_{tu}^k) \leq 0$, is implemented as follows:

$$f\left(x_{tu}^k\right) - f(x^*) \leq TOLT \cdot (1 + |f(x^*)|) \tag{17}$$

where precision *TOLT* is to be selected by the user. This parameter is closely related to the tolerance *TOLEV* for considering minima to be at the same level of the objective function value. First we will derive some bounds for *TOLEV*.

Suppose x_1^* and x_2^* are two *different* minima at the same level, i.e. $f(x_1^*) = f(x_2^*)$ and $x_1^* \neq x_2^*$ and x_1^{k+1} and x_2^{k+1} are their respective approximations that satisfy the criteria:

$$|f(x_i^{k+1}) - f(x_i^k)| \leq TOLF \cdot (1 + |f(x_i^{k+1})|), \quad i = 1, 2 \tag{18}$$

If the function is well conditioned, the right hand side of Eq. (17) is a bound for the error on the function values of the exact solutions and the approximated ones, so we have that

$$|f(x_1^{k+1}) - f(x_1^k)| \leq TOLF \cdot (1 + \max(|f(x_1^{k+1})|, |f(x_2^{k+1})|)) \tag{19}$$

and the same inequality applies for x_2^{k+1}.

As $f(x_1^*) = f(x_2^*) = f^*$ it follows that

$$|f(x_1^{k+1}) - f(x_2^{k+1})| \leq 2 \cdot TOLF \cdot (1 + \max(|f(x_1^{k+1})|, |f(x_2^{k+1})|)) \tag{20}$$

thus the relative error between the two minima at the same level will be utmost $2 \cdot TOLF$. In our code we have selected

$$TOLEV = TOLF \tag{21}$$

and the reason will be clear soon after.

In order to properly describe the tolerance *TOLT* for a successful tunnelization, it is necessary to clarify its relation to other tolerances. When the problem to be solved has many local minima at the same level (within the tolerance *TOLEV*), the performance of the algorithm improves, generally, if these minima are detected and destroyed using poles. So, in order to be able to find and destroy those local minima, the following inequality has to be satisfied (see Fig. 1):

$$TOLT \geq TOLEV \tag{22}$$

Also, to guarantee that the point x_{tu}^* is effective in another valley, another condition for *TOLT* will be

$$TOLT \leq TOLF \tag{23}$$

then the relation between the three tolerances will be

$$-2 \cdot TOLF \leq TOLEV \leq TOLT \tag{24}$$

We have implemented here

TOLT = *TOLF* to allow the method to find local minima at the same level.

Also we must have *TOLEV* = min(|*TOLT*|, *TOLF*); this justifies the choice in Eq. (21).

These tolerances allow us to successfully find all the minima at the same level.

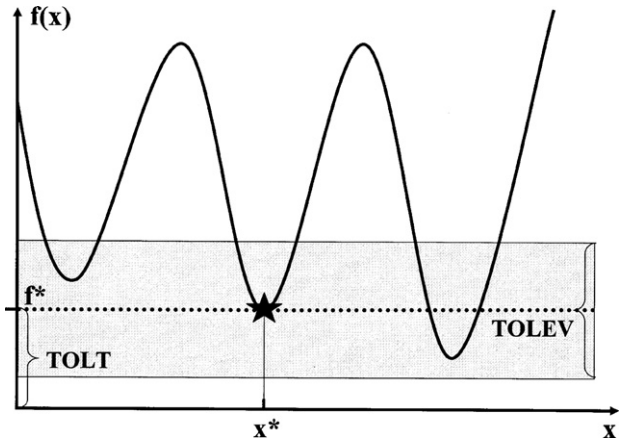

Fig. 1. Tolerances for searching multiple minima at the same level.

3.4. General stopping conditions

The algorithm stops when any of the following criteria is satisfied:

(1) In the tunneling phase, the given maximum number of initial points to start the search for x_{tu} has been reached. The minima at the same level (known) found are the putative global minima.
(2) All the global minima at the same level required by the user, have been found.
(3) The given maximum number of function evaluations has been reached.

4. Results

The ability of the tunneling global optimization method in finding all minima of the modified objective function with $\Phi = 0$ is tested for several mixtures, including very difficult conditions. Problems 1–5 are benchmark problems for phase stability (taken from Ref. [5]), Problem 6 is from Sun and Seider [6], and Problem 7 is for a quaternary mixture of Kohse and Heidemann [35], studied by Sun and Seider [6] and Zhu et al. [9].

There are two stopping criteria for the minimization routine. The first is given by

$$\frac{(\Phi_\nu - \Phi_{\nu+1})}{\max(|\Phi_{\nu+1}|, |\Phi_\nu|, 1)} < FACTR * EPSMACH \tag{25}$$

where *EPSMACH* is the machine precision (automatically generated by the code), *FACTR* is provided by the user to get desired tolerance, and ν designates the iteration level.

The second criterion checks the norm of projected gradients

$$\max_{j=2,nc} \left\| proj\left(\frac{\partial \Phi}{\partial x_j}\right) \right\| \leq PGTOL \tag{26}$$

where *PGTOL* is the required tolerance for the norm of projected gradients.

The first stopping condition is applied to check if the objective function has no further decrease, and the second to guarantee that the iterate is the optimal point. Both conditions are used in the minimization phase. It should be emphasized that the same local optimization routine is used here for both phases: minimization and tunnelization. In the minimization phase a local minimum of the original objective function is found. In the tunneling phase, a point in another valley is located. In both phases, a descent direction is generated and the magnitude of the step in this direction is computed using a line search routine. In the tunneling phase the first stopping condition checks if the tunneling function has sufficient decrease, and uses a mobile pole to force further decrease, if the condition is not satisfied. As in this phase we are *not* looking for the minimum of the tunneling function, but only for a point where the tunneling function is less than or equal to zero, the second condition is not used in this phase.

We use in all examples very strict tolerances. We consider *FACTR* = 1.d + 2, corresponding to a high accuracy, and the tolerance associated with the projected norm of the gradient vector *PGTOL* is set at 1.d − 8. The value of the objective function at the global minima is set at 1.d − 12.

It would be very useful to provide the code the maximum number of stationary points (to avoid the last tunneling phase). The number of stationary points of Φ is not known *a priori*. Wasylkiewicz et al. [18] proposed a topological criterion for stationary points relating the number of minima, maxima and saddles in the case of liquid–liquid equilibrium. Unfortunately, this criterion is not valid for systems involving vapor and liquid phases [36]. Sofyan et al. [37] state that the number of stationary points is always an odd number. This is not correct and the number of stationary points can be even; for example, there are two stationary points (a minimum and a saddle) for binary mixtures at pressure and temperature conditions between phase boundaries and the limit of stability testing (see [38]). Starting from the observation that in binary mixtures the minima correspond to equilibrium phases or to incipient phases (near phase boundaries), and admitting that maximum three-phase may form, we can set the maximum number of stationary points for binary mixtures ($n = 1$) at $nlev = 5$ (three minima separated by two maxima). For $n > 1$ ($nc > 2$) the maximum number of stationary points should not be restricted; however, in some examples we present the results for an imposed *nlev*, then give separately the number of function evaluations for the last tunneling phase.

The tunneling method eventually converges to the global minimum for any initial guess in the feasible region. One may use of course the same initialization as for the TPD function.

We use the two-sided initialization of Michelsen [3], as implemented by Nichita et al. [11]. The two initialization types are denoted here as V initialization (for a vapor-type trial phase with $x_i^{(0)} = z_i K_i$) and L initialization (for a liquid-type trial phase with $x_i^{(0)} = z_i / K_i$). The equilibrium constants are estimated using Wilson's [39] relation.

However, for the modified objective function, one of the minima known in advance is the trivial solution (TS) which is, always among the desired solutions (it will be visited anyway at some stage of the calculations), thus we can start at the trivial solution, then proceed with the tunneling phase for searching the other minima. Initialization at TS avoids finding first a local minimum with $\Phi > 0$ in some cases. Hua et al. [5] also discussed the possibility of discarding intervals containing the TS.

Here we report results using the three initializations mentioned above.

4.1. Problem 1: methane–hydrogen sulphide binary mixture

Testing phase stability for the methane (1)–hydrogen sulphide (2) binary mixture at $p = 40.53$ bar and $T = 190$ K is known in the literature to be a highly difficult problem [3–6,11,12,14,40,20]. The SRK EoS is used with the binary interaction parameter (BIP) $k_{12} = 0.08$. Six feeds are considered, and results are given in Table 1: feed composition, stationary points, value of k^* at each stationary point (which equals $\bar{D}$), the number of function and gradient evaluations (NFGE) for different initializations, and the state of the mixture. Note that obviously, the order in which global minima are found is different for each initialization option (in Tables 1–6, the stationary points are listed in the order corresponding to L initialization). The maximum number of global minima for this example is taken as $nlev = 5$.

In Fig. 2a the objective function is represented for the equimolar mixture, with a detail for high methane concentrations in Fig. 2b. The main difficulty from the optimization point of view of this problem is the fact that one of the valleys has a very sharp shape, whereas for instance at the trivial solution valley its neighbourhood is very flat. Both kinds of problems are known to be difficult for local optimization gradient-based methods.

For feeds 2–6 there is an interval (from about 0.954 to about 0.978 methane mole fraction) for which the cubic EoS has three distinct real roots; the fifth stationary point reported by Sun and Seider [6], Hua et al. [4,5], and Balogh et al. [20] (with a methane mole fraction of about 0.97) corresponds to Z_{int} (the intermediary value of the compressibility factor among the three real roots of the cubic EoS), as can be seen also on a TPD plot, for instance Fig. 2 from Ref. [11]. These kinds of stationary points are not found by our method since only the root giving the lowest Gibbs free energy is considered. However, these minima are not of importance for assessing the phase status or initializing a phase split.

For feed 1, the local minimum with $\Phi > 0$ can or cannot be captured, depending on initialization (such a local minimum is found only if the initialization point is located in the basin attraction of this solution for the local minimization method; obviously, tunnel-

Table 1
Problem 1: C_1 (1)/H_2S (2) at $p = 40.53$ bar and $T = 190$ K (SRK EoS).

Feed	Feed composition	Zeros of $\Phi(x)$	$k^*(\bar{D})$	NFGE (Init. = L)	NFGE (Init. = V)	NFGE (Init. at TS)	State
					(M1 + T1 + M2 + T2 + M3 + T3 + M4 + T4)		
1	(0.9885, 0.0115)	(0.988500, 0.011500) (0.967419, 0.032581)	0 0.013041	1406(8 + 19 + 8 + 8 + 2 + 1361)[a]	1081(11 + 20 + 2 + 1048)	1276(1 + 122 + 2 + 1151)	Stable
2	(0.9813, 0.0187)	(0.981300, 0.018700) (0.923314, 0.076686) (0.509467, 0.490533) (0.115207, 0.884793)	0 −0.003957 0.072974 0.010909	827(12 + 16 + 0 + 16 + 3 + 617 + 3 + 160)	745(11 + 39 + 2 + 58 + 2 + 117 + 2 + 514)	974(1 + 37 + 2 + 58 + 2 + 656 + 2 + 216)	Unstable
3	(0.93, 0.07)	(0.982164, 0.017836) (0.93, 0.07) (0.477089, 0.522911) (0.125733, 0.874267)	0.001472 0 0.096508 0.051296	957(9 + 7 + 2 + 24 + 0 + 527 + 0 + 388)	594(11 + 11 + 2 + 16 + 2 + 52 + 2 + 498)	830(1 + 10 + 0 + 11 + 2 + 497 + 2 + 307)	Stable
4	(0.50, 0.50)	(0.925382, 0.074618) (0.50, 0.50) (0.118133, 0.881867) (0.981560, 0.018440)	−0.082521 0 −0.056893 −0.079325	902(8 + 9 + 2 + 22 + 2 + 484 + 2 + 375)	604(10 + 12 + 2 + 19 + 2 + 54 + 2 + 505)	896(1 + 10 + 2 + 23 + 2 + 510 + 3 + 345)	Unstable
5	(0.112, 0.888)	(0.980996, 0.019004) (0.920821, 0.079179) (0.520317, 0.479683) (0.112, 0.888)	0.002401 −0.002462 0.068221 0	832(8 + 11 + 2 + 22 + 2 + 442 + 2 + 343)	877(11 + 7 + 2 + 12 + 2 + 455 + 2 + 386)	816(1 + 15 + 2 + 16 + 2 + 536 + 2 + 242)	Unstable
6	(0.11, 0.89)	(0.980796, 0.019204) (0.919131, 0.080869) (0.527382, 0.472618) (0.11, 0.89)	0.011078 0.005608 0.072356 0	908(7 + 12 + 0 + 22 + 2 + 515 + 2 + 348)	820(11 + 8 + 2 + 13 + 2 + 496 + 2 + 286)	857(1 + 15 + 2 + 16 + 2 + 536 + 2 + 283)	Stable

[a] Local minimum with $\Phi = 0.104068$ at $x = (0.257773, 0.742227)$ first found.

Table 2
Problem 2: C_1 (1)/C_3 (2) at $p = 100$ bar and $T = 277.6$ K (SRK EoS).

Feed	Feed composition	Zeros of $\Phi(x)$	$k^*(\bar{D})$	NFGE (Init. = L)	NFGE (Init. = V) (M1 + T1 + M2 + T2 + M3 + T3)	NFGE (Init. at TS)	State
1	(0.40, 0.60)	(0.40, 0.60)	0	855(8 + 847)	824(8 + 816)	836(1 + 835)	Stable
2	(0.68, 0.32)	(0.68, 0.32) (0.687719, 0.312281) (0.772465, 0.227535)	0 −3.6e−7 −0.000335	1733(16 + 8 + 2 + 28 + 2 + 1677)	1750(20 + 8 + 1 + 28 + 1 + 1692)	1716(1 + 8 + 1 + 30 + 1 + 1675)	Unstable
3	(0.73, 0.27)	(0.650287, 0.349713) (0.73, 0.27) (0.757048, 0.242952)	−0.000295 0 −2.081e−5	1520(12 + 9 + 1 + 28 + 1 + 1469)	1503(13 + 9 + 1 + 27 + 1 + 1452)	1534(1 + 7 + 2 + 37 + 2 + 1485)	Unstable
4	(0.90, 0.10)	(0.90, 0.10)	0	1371(15 + 1356)	1352(10 + 1342)	1272(1 + 1271)	Stable

ing will not find a stationary point with $\Phi > 0$ after finding a first global minimum of Φ). It is located at $x_1 = 0.2578$, with $k_1 = 0.2078$, $k_2 = 0.4360$, and the value of the objective function is $\Phi = 0.1041$. This stationary point of Φ with $k_1 \neq k_2$ (this means that the hyperplane tangent to Gibbs free energy surface cannot be parallel with the hyperplane at $\boldsymbol{z}$) is not a stationary point of $\bar{D}$; it corresponds to an inflexion point of $\bar{D}$, and the current pressure is above the limit of stability testing (LST, also named limit of parallel tangent [41], or "shadow curve" [42]), in the region where only the trivial solution exists. This feature is also discussed by Sun and Seider [6]. In the single phase region, global minima with $k^* > 0$ exist only between the phase boundary and the LST; on the LST, a non-trivial stationary point of TPD is a saddle point.

The minimum corresponding to Z_{int} is at $x_1 = 0.9763$, with $k_1 = k_2 = 1.281$. Fig. 3a and b shows the objective function for this feed. In Fig. 4 the TPD function is represented, showing that the branch of the intermediary value of Z is not corresponding to the minimum Gibbs free energy; this is the reason why apparently a solution found by other authors is missed.

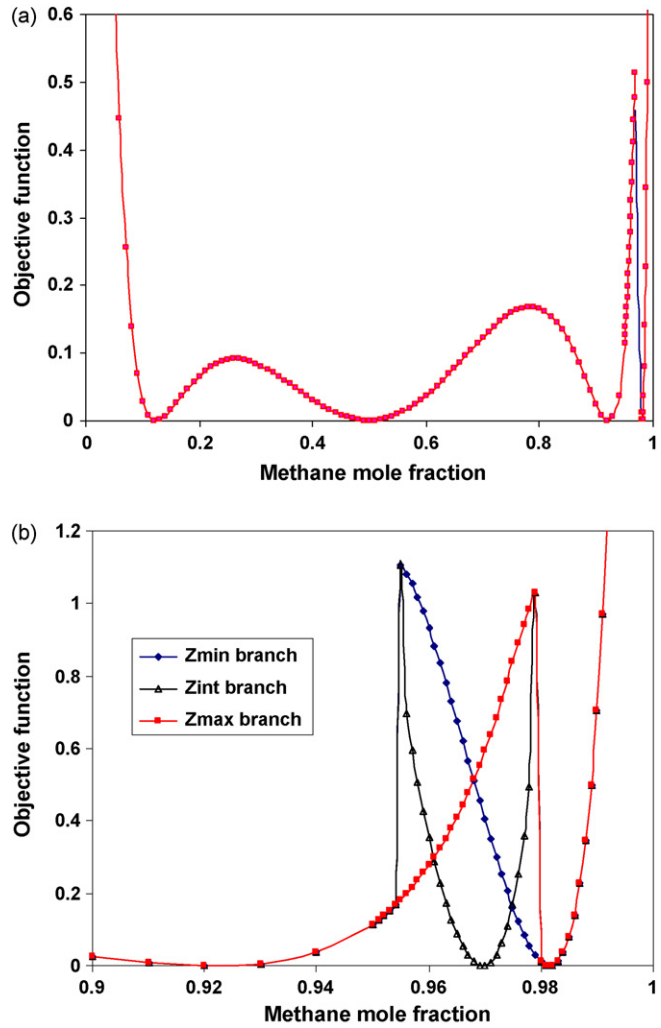

Fig. 2. (a) Objective function for the equimolar C_1/H_2S mixture ($p = 40.53$ bar and $T = 190$ K). (b) Objective function for the equimolar C_1/H_2S mixture ($p = 40.53$ bar and $T = 190$ K). Detail.

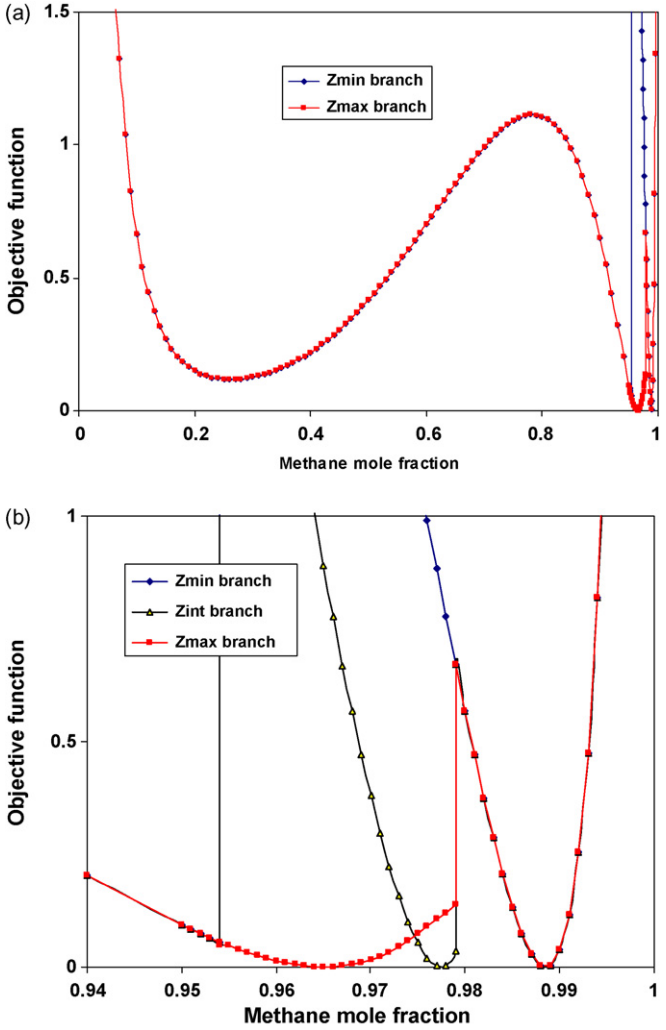

Fig. 3. (a) Objective function for the C_1/H_2S mixture (feed 1, $p = 40.53$ bar and $T = 190$ K). (b) Objective function for the C_1/H_2S mixture (feed 1, $p = 40.53$ bar and $T = 190$ K). Detail.

Table 3
Problem 3: C_2 (1)/N_2 (2) at $p = 76$ bar and $T = 270$ K (PR EoS).

Feed	Feed composition	Zeros of $\Phi(x)$	$k^*(\bar{D})$	NFGE (Init. = L)	NFGE (Init. = V)	NFGE (Init. at TS)	State
				(M1 + T1 + M2 + T2 + M3 + T3)			
1	(0.90, 0.10)	(0.90, 0.10)	0	1039(10 + 1029)	1862(9 + 312 + 7 + 1534)[a]	987(1 + 986)	Stable
2	(0.82, 0.18)	(0.505590, 0.494410) (0.82, 0.18) (0.703950, 0.296050)	−0.009746 0 0.005789	2067(11 + 9 + 2 + 235 + 2 + 1808)	2099(11 + 9 + 2 + 235 + 2 + 1840)	2073(1 + 7 + 0 + 235 + 2 + 1828)	Unstable
3	(0.70, 0.30)	(0.510582, 0.489418) (0.823275, 0.176725) (0.70, 0.30)	−0.013792 −0.006865 0	2309(11 + 11 + 2 + 240 + 0 + 2045)	2187(10 + 11 + 2 + 240 + 0 + 1924)	2229(1 + 10 + 2 + 255 + 2 + 1959)	Unstable
4	(0.56, 0.44)	(0.56, 0.44) (0.664692, 0.335308) (0.845281, 0.154719)	0 0.002643 −0.015530	1960(11 + 7 + 2 + 30 + 2 + 1908)	1935(12 + 7 + 2 + 29 + 2 + 1883)	1903(1 + 7 + 2 + 29 + 2 + 1862)	Unstable
5	(0.40, 0.60)	(0.40, 0.60)	0	2252(7 + 3 + 7 + 2235)[a]	1568(7 + 1561)	1573(1 + 1572)	Stable

[a] Local minimum with $\Phi > 0$ first found.

Table 4
Problem 4: C_1 (1)/CO_2 (2) at $p = 60.8$ bar and $T = 220$ K (PR EoS).

Feed	Feed composition	Zeros of $\Phi(x)$	$k^*(\bar{D})$	NFGE (Init. = L)	NFGE (Init. = V)	NFGE (Init. at TS)	State
				(M1 + T1 + M2 + T2 + M3 + T3)			
1	(0.90, 0.10)	(0.90, 0.10)	0	1321(15 + 1306)	1348(9 + 1339)	1313(1 + 1312)	Stable
2	(0.80, 0.20)	(0.502644, 0.497356) (0.741188, 0.258812) (0.80, 0.20)	−0.007427 0.002206 0	2720(9 + 15 + 2 + 1086 + 2 + 1606)	2730(8 + 18 + 2 + 1112 + 2 + 1588)	2479(1 + 7 + 1 + 1182 + 2 + 1286)	Unstable
3	(0.70, 0.30)	(0.642304, 0.35769) (0.70, 0.30) (0.815263, 0.184737)	−0.000188 0 −0.007004	2563(12 + 10 + 1 + 707 + 2 + 1831)	2556(12 + 10 + 1 + 677 + 2 + 1854)	2522(1 + 8 + 1 + 693 + 1 + 1818)	Unstable
4	(0.57, 0.43)	(0.57, 0.43) (0.726852, 0.273148) (0.808873, 0.191127)	0 0.003164 −0.001310	2910(9 + 15 + 2 + 1305 + 2 + 1577)	2499(9 + 15 + 2 + 1253 + 1 + 1219)	2775(1 + 15 + 2 + 1239 + 2 + 1516)	Unstable
5	(0.40, 0.60)	(0.40, 0.60)	0	1574(12 + 1562)	1545(12 + 1533)	1607(1 + 1605)	Stable

Table 5
Problem 5: C_1 (1)/C_2 (2)/N_2 (3) at $p = 76$ bar and $T = 270$ K (PR EoS).

Feed	Feed composition	Zeros of $\Phi(x)$	$k^*(\tilde{D})$	NFGE (Init. = L)	NFGE (Init. = V)	NFGE (Init. at TS)	State
				(M1 + T1 + M2 + T2 + M3 + T3)			
1	(0.1, 0.6, 0.3)	(0.101616, 0.586724, 0.311659) (0.1, 0.6, 0.3) (0.067797, 0.799168, 0.133035)	−5.889e−6 0 −0.014829	4352(17 + 49 + 2 + 611 + 7 + 3666)	4817(30 + 72 + 2 + 312 + 0 + 4401)	4800(1 + 63 + 2 + 306 + 2 + 4426)	Unstable
2	(0.30, 0.55, 0.15)	(0.245094, 0.658130, 0.096776) (0.30, 0.55, 0.15) (0.297372, 0.555600, 0.147028)	−0.001175 0 3.395e−7	4679(27 + 35 + 2 + 1645 + 2 + 2968)	4493(31 + 45 + 2 + 1273 + 2 + 3140)	4442(1 + 45 + 10 + 1245 + 2 + 3139)	Unstable
3	(0.38, 0.54, 0.08)	(0.38, 0.54, 0.08)	0	4488(36 + 4452)	4425(27 + 4398)	4457(1 + 4456)	Stable
4	(0.05, 0.90, 0.05)	(0.05, 0.90, 0.05)	0	3070(17 + 3053)	3127(13 + 118 + 17 + 2979)[a]	**3060(1 + 3059)**	**Stable**

[a] Local minimum with $\Phi > 0$ first found.

Table 6
Problem 6: C_1 (1)/CO_2 (2)/H_2S (3) (PR EoS).

Feed	Feed (z_1, z_2, z_3), T (K)/p (bar)	Zeros of $\Phi(x)$	$k^*(\tilde{D})$	NFGE (Init. = L)	NFGE (Init. = V)	NFGE (Init. at TS)	State
				(M1 + T1 + M2 + T2 + M3 + T3 + M4 + T4 + M5)			
1	(0.4989, 0.0988, 0.4023) 208.5/55.1	(0.919390, 0.034316, 0.046294) (0.244825, 0.091250, 0.663925) (0.4989, 0.0988, 0.4023) (0.817398, 0.059947, 0.122655) (0.858944, 0.050589, 0.090466)	−0.014587 −0.006804 0 −0.009693 −0.009446	3148(15 + 21 + 3 + 390 + 1 + 883 + 1 + 1832 + 2)	3162(17 + 20 + 1 + 835 + 2 + 670 + 2 + 1614 + 1)	2980(1 + 17 + 8 + 817 + 1 + 403 + 2 + 1729 + 2)	Unstable
2	(0.4989, 0.0988, 0.4023) 210.5/57.5	(0.911403, 0.036794, 0.051803) (0.255085, 0.092335, 0.652580) (0.4989, 0.0988, 0.4023)	−0.013474 −0.005710 0	3286(19 + 19 + 1 + 386 + 2 + 2859)	3024(16 + 19 + 1 + 287 + 2 + 2699)	3115(1 + 21 + 1 + 327 + 2 + 2763)	Unstable
3	(0.48, 0.12, 0.40) 210.5/57.5	(0.902932, 0.044559, 0.052509) (0.289802, 0.116631, 0.593567) (0.48, 0.12, 0.40) (0.766632, 0.081445, 0.151923) (0.861572, 0.057381, 0.081047	−0.005454 −0.002238 0 −0.005460 −0.003710	3245(17 + 22 + 3 + 423 + 1 + 611 + 1 + 2167 + 2)	3388(19 + 17 + 2 + 438 + 2 + 1193 + 1 + 1714 + 2)	2946(1 + 17 + 1 + 520 + 0 + 932 + 2 + 1472 + 1)	Unstable
4	(0.4989, 0.0988, 0.4023) 227.55/48.6	(0.900477, 0.040822, 0.058701) (0.4989, 0.0988, 0.4023) (0.277888, 0.094488, 0.627624)	−0.184860 0 −0.005152	4138(16 + 161 + 3 + 817 + 2 + 3239)	3956(12 + 18 + 1 + 362 + 1 + 3562)	3762(1 + 18 + 1 + 305 + 1 + 3436)	Unstable

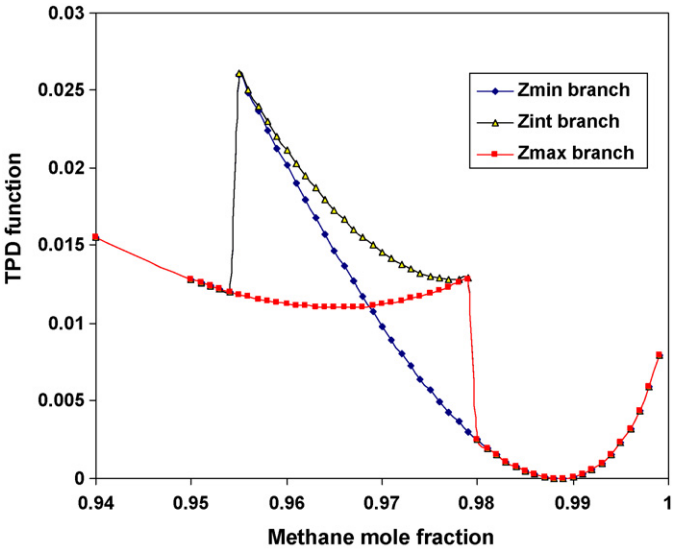

Fig. 4. TPD function for the C_1/H_2S mixture (feed 1, $p = 40.53$ bar and $T = 190$ K).

For comparison in terms of efficiency, the stability routine in the code TUNPEQ [11] requires 500–700 NFGE for feeds 1–6 to find (and validate) only the global minimum of the TPD function (without finding all stationary points). For all selected feeds, there are maximum four global minima of Φ; fourth tunneling phase ensures that there are not additional global minima.

4.2. Problem 2: methane–propane binary mixture

The binary mixture methane (1)–propane (2) is studied with the SRK EoS (with $k_{12} = 0.029$) at $p = 100$ bar and $T = 277.6$ K for four feeds. Results are given in Table 2. Feeds 2 and 3 are difficult ones at these conditions. The objective function for feed 2 is plotted in Fig. 5a, with a detail in Fig. 5b. For feed 2, the minimum near the trivial solution corresponds to a small positive maximum of the TPD function. Note the extremely small value (about 10^{-8}) for the maximum of Φ separating the two close minima, which makes this problem a difficult one. For both unstable feeds, the points defined by test temperature and pressure are located inside the spinodal curve (two global minima with $k^* < 0$).

4.3. Problem 3: ethane–nitrogen binary mixture

This is a mixture of ethane (1) and nitrogen (2) at $p = 76$ bar and $T = 270$ K. The PR EoS is used with $k_{12} = 0.08$. Results for the five feeds (two stable and three unstable) studied by Hua et al. [5] are given in Table 3. For the stable feeds, a local minimum with $\Phi > 0$ (with $k_1 \neq k_2$, thus these are not stationary points of the TPD function) is first found in two cases. They are located at $x_1 = 0.617189$ for feed 1, and at $x_1 = 0.763015$ for feed 5. For feeds 2 and 4 test points are located between spinodal and saturation curves (only one minimum with $k^* < 0$), while for feed 3 the test point is inside the spinodal curve.

4.4. Problem 4: methane–carbon dioxide binary mixture

This is a mixture of methane (1) and carbon dioxide (2) at $p = 60.8$ bar and $T = 220$ K. We use the PR EoS with $k_{12} = 0.095$. Results are presented in Table 4 for five feeds (from Ref. [5], two stable and three unstable). Note the increased number of NFGE in the second tunneling phase (to reach the valley of the third global minimum) as compared to previous binary examples.

4.5. Problem 5: methane–ethane–nitrogen ternary mixture

Stability testing for the methane (1)–ethane (2)–nitrogen (3) ternary mixture at $T = 270$ K and $p = 76$ bar (see results in Table 5) may be quite difficult for some feeds. The PR EoS is used, with $k_{12} = 0.021$, $k_{13} = 0.038$, and $k_{23} = 0.08$. For feeds 1 and 2 (both unstable), the difficulty is given by a zero of the objective function (corresponding to a very small negative value of the TPD function) located in the very close proximity of the trivial solution. For feed 4 (stable), for one initialization (at TS) a local minimum with $\Phi = 0.8577$ is first found at $\mathbf{x}^* = (0.124182, 0.588054, 0.287764)^T$, with $k_1 \neq k_2 \neq k_3$, thus an additional minimization/tunnelization cycle is required.

4.6. Problem 6: methane–carbon dioxide–hydrogen sulphide ternary mixture

The phase stability of a ternary mixture of methane (1)–carbon dioxide (2)–hydrogen sulphide (3) is analyzed for the four cases studied by Sun and Seider [6]. The PR EoS is used (with T_c, p_c, ω and BIPs $k_{12} = 0.1005$, $k_{13} = 0.0755$, and $k_{23} = 0.0999$ taken from Ref. [37]). Results (for $nlev = 5$) are presented in Table 6. All feeds are unstable at given conditions. For two feeds (1 and 3), there are five stationary points: the TS and four with negative TPD; if *nlev* is unrestricted, a fifth tunneling phase takes between 3000 and 4000 NFGE to ascer-

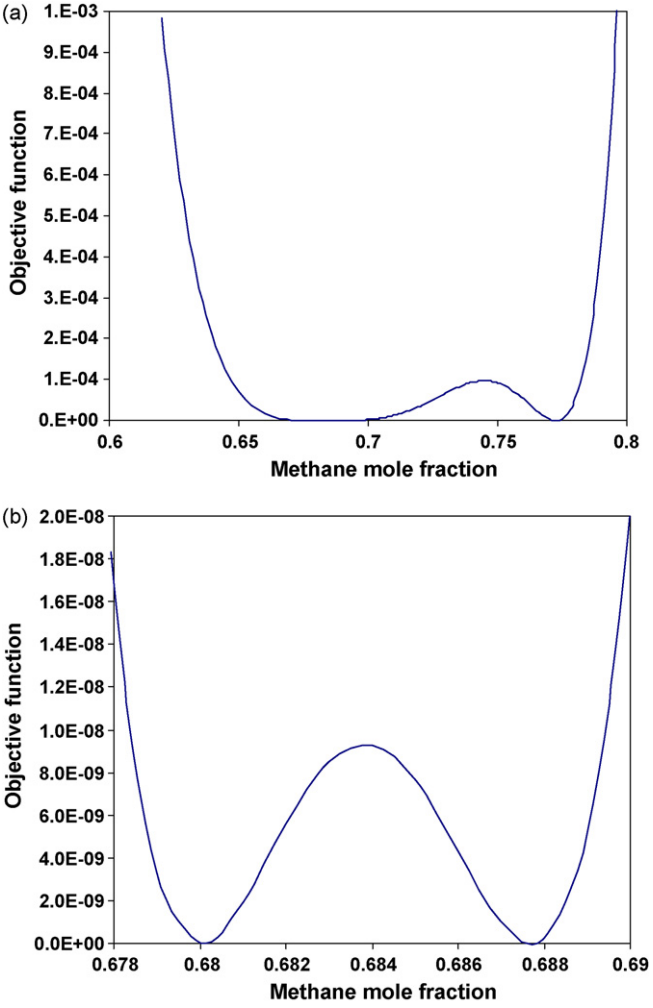

Fig. 5. (a) Objective function for the C_1/C_3 mixture (feed 2, $p = 100$ bar and $T = 277.6$ K). (b) Objective function for the C_1/C_3 mixture (feed 2, $p = 100$ bar and $T = 277.6$ K). Detail.

Table 7
Problem 7: flash of quaternary C_1 (1)/CO_2 (2)/nC_6 (3)/H_2S (4) at $p = 42.5$ bar and $T = 200$ K (SRK EoS and PR EoS).

Phase	Mole fractions, SRK EoS		Mole fractions, PR EoS	
	Component	Phase	Component	Phase
L_1	(0.48814649, 0.07397676, 0.05777089, 0.38010587)	0.394684	(0.52417338, 0.06961911, 0.04993429, 0.35627322)	0.473870
L_2	(0.17409520, 0.06436036, 0.01011867, 0.75142865)	0.260129	(0.18405194, 0.06113260, 0.00813007, 0.74668539)	0.323767
V	(0.95045598, 0.02301266, 0.00002280, 0.02650856)	0.345186	(0.94888913, 0.02281486, 0.00002671, 0.02826930)	0.202363

Table 8
Problem 7: quaternary C_1 (1)/CO_2 (2)/nC_6 (3)/H_2S (4) at $p = 42.5$ bar and $T = 200$ K (SRK EoS and PR EoS).

Feed	EoS	Zeros of $\Phi(x)$	$k^*(\bar{D})$	NFGE (Init. = V): (M1 + T1 + M2 + T2 + M3 + T3 + M4 + T4 + M5)/(T5)	State
L_1	SRK	(0.488146, 0.073977, 0.057771, 0.380106)	0	5169(33 + 118 + 2 + 32 + 3 + 1814 + 2 + 3163 + 2)/(4583)	Stable
		(0.891417, 0.038885, 0.001802, 0.067897)	0.039073		
		(0.310236, 0.075075, 0.033354,0.058134)	0.002755		
		(0.174095, 0.064360, 0.010119, 0.751429)	0		
		(0.950456, 0.023013, 0.000023, 0.026509)	0		
L_1	PR	(0.524173, 0.069619, 0.049934, 0.356273)	0	5304(29 + 102 + 2 + 49 + 2 + 1698 + 3 + 3417 + 2)/(4179)	Stable
		(0.332311, 0.071630, 0.028868, 0.567191)	0.003203		
		(0.184052, 0.061133, 0.008130, 0.746685)	0		
		(0.894835, 0.036643, 0.001508, 0.067014)	0.037848		
		(0.948889, 0.022815, 0.000027, 0.028269)	0		

tain globality for feeds 1 and 3. For feed 1, three of the stationary points with $k^* < 0$ are very close to one another.

The results are practically identical with those reported by Sofyan et al. [37], and close to those of Sun and Seider [6] obtained with HOMPEQ (the difference is due to different component properties and BIPs). The number of NFGE is much lower than IN/GB root inclusion tests, but slightly higher than for PEC [37]. For the first feed, Balogh et al. [43] reported preliminary results with the modified objective function and their stochastic method, which requires an average of 15,686 function evaluations but it is finding only four stationary points.

4.7. Problem 7: methane–carbon dioxide–normal-hexane–hydrogen sulphide quaternary mixture

This quaternary mixture of methane (1)–carbon dioxide (2)–normal-hexane (3)–hydrogen sulphide (4) was studied first by Kohse and Heidemann [35]. The problem addressed here was given by Sun and Seider [6], and later analyzed also by Zhu et al. [9], and Burgos-Solorzano et al. [44]. We want to validate using the phase stability routine the correct equilibrium state for a feed composition $\boldsymbol{z} = (0.5000, 0.0574, 0.0263, 0.4163)^T$ at $T = 200$ K and $p = 42.5$ bar. These conditions are difficult due to the proximity of a tri-critical point. Pure component properties (T_c, p_c, and ω) and BIPs ($k_{12} = 0.12$, $k_{13} = 0$, $k_{14} = 0.08$, $k_{23} = 0.15$, $k_{24} = 0.12$, $k_{34} = 0.06$) are taken from Burgos-Solorzano et al. [44] (Table 9, Model B).

First the feed is found to be unstable at given T and p, with negative values of the TPD function at the global minimum, for both EoS and SRK (with $k^* = -0.045536$) and PR (with $k^* = -0.029378$). The results of three-phase flash calculations performed with the code TUNPEQ [11] are listed in Table 7. Then, the stability of one of the equilibrium phases (L_1, the hydrocarbon-rich liquid phase) is analyzed (see Table 8, results for $nlev = 5$). The phase is stable indicating a correct three-phase split. Five stationary points are found; a fifth tunneling phase (T5) is checking for globality (number of NFGE given in parenthesis in Table 8). Note that it is sufficient to check the stability of only one equilibrium phase to validate the results of flash calculations.

Surprisingly, the results obtained with the PR EoS are practically identical to those reported by Burgos-Solorzano et al. [44] for the SRK EoS (three-phase split and the five stationary points). On the other hand, the results we obtain using the SRK EoS are close to those reported in Table 4 from Zhu et al. [9]. Apparently, Burgos-Solorzano et al. [44] have used the PR EoS.

For this problem, simulated annealing requires 19,300 function evaluations [9] only to find the global minimum of the TPD function (SRK EoS), while tunneling needs only 5169 NFGE to find all stationary points. For the Newton-Interval method, Burgos-Solorzano et al. [44] report 109 s to solve this problem (all stationary points), while tunneling gives the correct answer in just a few seconds.

5. Discussion

In our previous work on phase stability [11–15], we have already used the tunneling method to find (only) the global minimum of the TPD function. In this work tunneling finds *all* stationary points of the modified objective function with $\Phi = 0$, which correspond to the stationary points of the TPD function. Note that we exploit the fact that the value of the objective function at its global minima is known *a priori* (this is a required input data in our code); this information is not used by most methods. In fact, using the tunneling method is almost a natural choice for solving $\Phi = 0$. The unique feature of finding multiple global minima at the same level is exactly what is required by the structural properties of the function Φ.

In most practical cases, the purpose of stability analysis is to find only the global minimum; or, rather, to verify that the global minimum is non-negative. If only the state (stable or unstable) of a mixture at given conditions needs to be known, stability analysis can be abandoned whenever a negative value of the TPD function has been located. However, if all stationary points are known, an initialization scheme for multiphase equilibrium calculations that use this information may be better than one using only the global minimum (or the minimum with the largest negative value, which may not be the global minimum). It is known that the minima of the TPD function closely approximate the phase compositions at equilibrium; therefore, they are extremely good initial estimates for the minimization of Gibbs energy to solve the phase split problem.

Several ways of exploiting the knowledge of all stationary points of the TPD function for initializing phase split calculations have been presented in the literature. In a series of papers, Stateva and co-workers detailed how to use this information for solving various phase splits. They use stability results (all zeros of the function Φ) for initializing vapor–liquid–liquid equilibrium [21], phase equilibrium calculations for chemically reacting systems [22,45], and

liquid–liquid–liquid equilibrium [23]. Sun and Seider [6] found all stationary points by a homotopy continuation method, and then used trial-phase composition as initial estimates for searching the global minimum of the Gibbs free energy. In their approach, the larger number of phases is considered first, then the number of phases is reduced successively until the global solution (validated by a final stability check) is found. Wasylkiewicz et al. [18] proposed an approach based on ideas from differential geometry and the theory of differential equations to calculate all stationary points of the TPD function, and presented an algorithm for phase equilibrium with multiple liquid phases. They also start with the maximum number of equilibrium liquid phases (assumed to be equal to the number of minima if not restricted by the phase rule), and repeat the calculation sequence by decreasing the number of phases until globality is ascertained. At each stage, all minima of the TPD function are used for flash initialization. Later, Wasylkiewicz and Ung [36] modified this method to handle the vapor phase and to account for chemical reactions. Hua et al. [46] proposed a combined stability/flash procedure. They are first finding all stationary points of the TPD function using the Newton-Interval method. Then, for the initial guess from stability, they use a local minimization to solve the phase split problem. The results are again tested for stability and the number of phases is increased until the global solution is found. Müller and Marquardt [47] calculated all stationary points by an interval Newton/bisection algorithm for flash initialization and illustrated by several examples the benefit of global stability analysis in dynamic process simulations. Sofyan et al. [37] also calculated all the stationary points of the TPD function; they presented three different algorithms for multiphase equilibrium calculations, and detailed how to use results from stability analysis for initialization in each case.

In all the above-mentioned approaches, either computational costly, or heuristic and less reliable methods (like starting the search from multiple initial guesses) were used. Thus, an efficient and reliable procedure for global stability analysis is very useful for speeding up calculation procedures mentioned above or similar ones.

The maximum number of global minima at the same level can be specified in the code in advance. For binary mixtures we set $nlev = 5$, as discussed earlier. In the cases when the number of global solutions is this maximum ($nlev$), the code will stop as soon as it has found all these minima, and as a consequence it will not spend any time checking for global optimality. However, in the cases when the number of global minima is less than the maximum, the code will continue the search for other minima until another of the general stopping conditions will be satisfied. The difference in the total computing time and the one spent to find all possible global minima is considered the price for checking global optimality.

In this application, all global minima (at the same level) are found during the tunnelization phase, satisfying condition (15) as an equality. This means that at the end of the tunneling phase the local minimum has been detected, and thus in the minimization phase zero, one or at most two function evaluations are needed to get the required precision. This explains why in many cases we report zero function evaluations for this phase.

The early tunneling phases require few NFGE to find a new valley of the objective function containing other putative minimum; in the subsequent tunneling phases, after several global minima have already been detected, the number of other valleys with minima at the same level is reducing, and thus the computational cost of these phases increases. This is especially true when finding the last global minimum.

The last tunneling phase (which checks that all global minima have been found) is most expensive (it can represent for some problems up to 98% of the total computational effort). This kind of price is paid, in different ways, by any global optimization method. However, as discussed earlier, in some cases this last tunneling phase can be avoided.

We can start with any initial estimates within the feasible region; the tunneling method will eventually find all global minima, being essentially self-starting. The examples are showing that using three different initial points (L, V, and TS initializations) the number of NFGE required to find all global minima is generally not very different.

The comparison with other methods in the literature, is difficult to be based on CPU time (it depends on many factors, such as machine, compiler, code, and stopping criteria), but the limited information about the reported number of function evaluations taken by other global methods, suggests that our method is faster than Newton-Interval, simulated annealing, or stochastic methods. It should be noticed that when comparing the number of NFGE one must take into account that the proposed method requires the derivative of the fugacity coefficient with respect to mole fractions; NFGE means here calculation of the objective function and of the gradient vector. By solving the phase stability problem using the function Φ one higher level of derivatives is introduced (the gradient vector of the TPD function requires only the fugacities). However, for cubic EoS these derivatives have relatively simple forms, can be calculated at a low cost once fugacities are available, and they are available in practically all simulation packages. The calculation of fugacity derivatives with respect to mole fractions in order to calculate analytically the gradient vector of Φ is another price to be paid for using the tunneling gradient-based method to minimize Φ. However, this price is not high at all; it is worth noting that tunneling finds all the stationary points of the objective function with almost the same computational effort than it finds the global minimum (by comparing the number of NFGE with those reported in our previous publications on solving the stability problem by using tunneling).

Regarding future work, the next step would be to use the parallel version of the tunneling method [34]. In the parallel version, as all the processors are searching for points in another valley (at the tunneling phase), from different initial points (first in a neighbourhood of the last local minimum and in the whole feasible region afterwards), they explore efficiently several regions of the feasible space simultaneously. The formulation of phase stability testing with the modified objective function is particularly suited for parallelization.

Another important phase equilibrium problem, somewhat similar in nature, namely mixture critical points calculation, can also be formulated as a global optimization problem (two-dimensional, with molar volume and temperature as primary variables) with multiple global minima at a known level. This approach is of interest for mixtures that may have several critical points, or no critical point at all. Finally, the formulation of the stability problem as treated here in terms of reduced variables [48] is currently being investigated.

6. Conclusions

The gradient-based tunneling global optimization method is used to find multiple global minima at the same level (known in advance, with $\Phi = 0$) for the phase stability problem with cubic two-parameter EoS. Any stationary point of the tangent plane distance function is a global minimum of the modified objective function. The tunneling method is able to find efficiently and reliably all minima of interest for a modified objective function for phase stability testing; the method proposed here for stability testing is faster than most global methods proposed in the literature. A variety of numerical experiments are carried out at difficult conditions, proving the ability of the tunneling method to solve the phase stability problem. While in our previous work on global optimization applied to phase equilibrium problems we have focused on finding only the

global minimum, in this work all stationary points of the objective function are found.

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