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A Dislocation Hyperbolic Augmented Lagrangian Algorithm for the Phase Stability Problem

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Abstract

In this work, we solve the tangent plane distance (TPD) minimization problem. This problem is a class of problems in the field of chemical engineering, and belongs to the class of constrained minimization problems (with differentiability and nonconvexity assumptions). The TPD problem is usually solved by interior point, Newton, and heuristic methods. In this work, we propose to consider a dislocation hyperbolic augmented Lagrangian algorithm (DHALA) to solve the problem, where DHALA belongs to the class of augmented Lagrangian methods. We present computational experiments, where we show that our algorithm is competitive (in terms of execution time) with respect to other augmented Lagrangian algorithms, in the resolution of the TPD problem, and obtained better solutions than approaches reported in the literature.

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Abstract

In this work, we solve the tangent plane distance (TPD) minimization problem. This problem is a class of problems in the field of chemical engineering, and belongs to the class of constrained minimization problems (with differentiability and nonconvexity assumptions). The TPD problem is usually solved by interior point, Newton, and heuristic methods. In this work, we propose to consider a dislocation hyperbolic augmented Lagrangian algorithm (DHALA) to solve the problem, where DHALA belongs to the class of augmented Lagrangian methods. We present computational experiments, where we show that our algorithm is competitive (in terms of execution time) with respect to other augmented Lagrangian algorithm, in the resolution of the TPD problem, and obtained better solutions than approaches reported in the literature.

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1. Introduction

We are interested in solving the constrained optimization model

$$\min_{x \in \mathbb{R}^n} f(x), \text{ s.t. } g(x) \leq 0, \quad c(x) = 0, \quad x \in \Omega, \quad (1.1)$$

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where $f : \mathbb{R}^n \rightarrow \mathbb{R}$, $g : \mathbb{R}^n \rightarrow \mathbb{R}^m$ and $c : \mathbb{R}^n \rightarrow \mathbb{R}^p$ are continuously differentiable, possibly nonconvex functions, $\Omega = \{x \in \mathbb{R}^n : a \leq x \leq b\}$ is a nonempty compact set, and is a box-constraint.

Why use augmented Lagrangian methods?

Augmented Lagrangian Algorithms (ALA) enforce constraints by adding a penalty term to the Lagrangian. This yields a sequence of box-constrained subproblems: each iteration solves a box-constrained minimization of the augmented Lagrangian, followed by an update of the Lagrange multipliers. ALA have proven to be very efficient in solving different kinds of problems in different areas of science and engineering, see the software packages LANCELOT [10] and ALGENCAN [8], and their respective citations. Both packages rely on a quadratic penalty component. In particular Birgin and Martínez [8] incorporated safeguarded multiplier updates. Prior works reported that ALGENCAN has strong computational performance and supports theoretical results for various mathematical models (see the works of Birgin and Martínez [8] and Birgin et al. [6]).

Some Previous Work on the Dislocation Hyperbolic Augmented Lagrangian Function

In 1982, the hyperbolic penalty function (HPF) was introduced as an approach for inequality-constrained optimization (see the work of Xavier [37]). The HPF includes a smoothing parameter related to the Zangwill penalty function [41]. It was later incorporated into augmented Lagrangian frameworks (see the work of Xavier [38]) and subsequently became known as the dislocation hyperbolic augmented Lagrangian function (DHALF) [29]. DHALF has since been investigated in several studies reporting theoretical properties and computational results. Representative contributions include:

- (a) Hyperbolic-penalty-based methods have been considered for min-sum-min problems [40] and clustering problem [39]. Variants of the HPF were later proposed and revisited in 2014 [12] and 2016 [33]. These works arise in global optimization and employ safeguarded multiplier-update strategies (similar in spirit to those used by Birgin and Martínez [8]). The resulting subproblems are solved using deterministic global optimization methods, such as DIRECT [26]. In particular, Costa et al. [12] reported that the modified HPF can outperform quadratic-penalty

approaches for certain problem classes, including comparisons with the penalty studied by Di Pillo et al. [14].

- (b) The HPF has also been studied under the name hyperbolic smoothing function (HSF) in the works by Bagirov and coauthors; applications include minimax problems [1], clusterwise linear regression [4], clustering problems [3, 2], and smoothing of a set of constraints [36].
- (c) Theoretical results for the DHALF include analyses under convexity assumptions [28] and in nonconvexity settings [29, 7]. Existence of saddle points in Euclidean spaces was established by Ramirez et al. [31], where second-order conditions were also discussed. Duality results in normed spaces are presented by Dolgopolik [16] (see Example 11).

Considering the discussion above, we are motivated to apply hyperbolic methodologies to a range of mathematical models. The main contributions of this work are as follows:

- Problem formulation and framework. We show that the TPD problem can be cast as an instance of problem in Eq. (1.1). The TPD has traditionally been addressed by Newton-type methods [23, 24, 9], trust-region approaches [27], Newton-Raphson methods [17], and quasi-Newton methods [35]. An multilocal penalty algorithm that combines exponential and hyperbolic penalty functions was proposed by Pereira et al. [25]. In this work, we instead adopt augmented Lagrangian strategies, the quadratic augmented Lagrangian algorithm (QALA) and the dislocation hyperbolic augmented Lagrangian algorithm (DHALA), and apply them to a representative set of TPD instances.
- Theoretical extensions and feasibility criteria. We address minimization problems with both inequality and equality constraints. We establish convergence results under nonconvex assumptions and introduce new feasibility conditions for our algorithm, distinct from those considered by Ramirez et al. [30]. Previous analyses of DHALA established convergence to local solutions (Karush-Kuhn-Tucker points) [28, 7, 29]. Here, we extend those theoretical results to the mixed-constraint setting.
- Computational performance on realistic instances. Our experiments indicate that DHALA achieves lower runtime on the TPD problem than a widely used augmented-Lagrangian-type method commonly cited in the literature. Earlier computational studies of DHALA focused on

small-scale instances and simplified tests; in contrast, we apply DHALA to a concrete problem arising in chemical engineering.

The work is organized as follows: Section 2 presents the proposed hyperbolic augmented Lagrangian algorithm for the TPD problem, establishes key properties of the underlying augmented Lagrangian function, and proves a convergence result; the section concludes with computational experiments illustrating the behavior of DHALA. Section 3 defines the TPD problem and reports computational results obtained with DHALA, along with a comparison against a well-known augmented Lagrangian algorithm. Section 4 summarizes our conclusions.

Notation: Some denotations that will be considered throughout this work are: If $x \in \mathbb{R}^n$, $x = (x_1, \dots, x_n)^T$. If $g : \mathbb{R}^n \rightarrow \mathbb{R}^m$, then $g(x)_+ = (\max\{0, g_1(x)\}, \max\{0, g_2(x)\}, \dots, \max\{0, g_m(x)\})$. The symbol $\|\cdot\|$ denotes the Euclidean norm, $\|\cdot\|_\infty = \max_{1 \leq i \leq n} |x_i|$ is the infinity norm, $\mathbb{R}_+^n = \{x \in \mathbb{R}^n : x \geq 0\}$ and $\mathbb{R}_{++}^n = \{x \in \mathbb{R}^n : x > 0\}$.

2. The Algorithm

We define the Dislocation Hyperbolic Augmented Lagrangian Function, by $\mathcal{L}_H : \mathbb{R}^n \times \mathbb{R}_+^m \times \mathbb{R}^p \times \mathbb{R}_{++} \rightarrow \mathbb{R}$,

$$\mathcal{L}_H(x, \lambda, \mu, \tau) = f(x) + \sum_{i=1}^m \frac{1}{\tau} h(\lambda_i g_i(x) \tau) + \sum_{j=1}^p \frac{\tau}{2} \left(c_j(x) + \frac{\mu_j}{\tau} \right)^2. \quad (2.2)$$

In Eq. (2.2), the function h is considered for inequality constraints, and the classical quadratic penalty function (QPF) is considered for equality constraints. The QPF is also considered in other algorithms [8, 21, 34]. On the other hand, we define $h : \mathbb{R} \rightarrow \mathbb{R}$, as $h(t) = t + \sqrt{t^2 + 1} - 1$. Some properties of the function h are:

- (P1) $h(0) = 0$ and $h'(0) = 1$.
- (P2) $h'(t) = 1 + \frac{t}{\sqrt{t^2 + 1}} > 0, \forall t \in \mathbb{R}$.

Next, we present our algorithm DHALA.

2.1. *Dislocation Hyperbolic Augmented Lagrangian Algorithm*

Step 0. Set $k = 1$. Let $(x^0, \lambda^0, \mu^0, \tau^0) \in \mathbb{R}^n \times \mathbb{R}_{++}^m \times \mathbb{R}^p \times \mathbb{R}_{++}$, $0 < \beta < 1$, and $1 < \alpha$. Define, $V_i^0 = \max\{g_i(x^0), 0\}$, $i = 1, \dots, m$. Choose a positive sequence $\{\epsilon^k\} \subset \mathbb{R}_+$ satisfying $\lim_{k \rightarrow \infty} \epsilon^k = \epsilon \geq 0$ and the convergence tolerance $\text{tol} > 0$.

Step 1. Find $x^k \in \Omega$ as an approximate global solution of the subproblem

$$\mathcal{L}_H(x^k, \lambda^k, \mu^k, \tau^k) \leq \mathcal{L}_H(x, \lambda^k, \mu^k, \tau^k) + \epsilon^k, \quad x \in \Omega. \quad (2.3)$$

Step 2. Updating of Lagrange multipliers:

$$\lambda_i^{k+1} = \lambda_i^k h'(\lambda_i^k g_i(x^k) \tau^k), \quad i = 1, \dots, m, \quad (2.4)$$

$$\mu_j^{k+1} = \mu_j^k + \tau^k c_j(x^k), \quad j = 1, \dots, p. \quad (2.5)$$

Step 3. Update the penalty parameter. Define

$$V_i^k = \lambda_i^k g_i(x^k), \quad i = 1, \dots, m.$$

If

$$\begin{aligned} & \max \{ \|g(x^k)_+\|_\infty, \|c(x^k)\|_\infty, \|V^k\|_\infty \} \\ & \leq \beta \max \{ \|g(x^{k-1})_+\|_\infty, \|c(x^{k-1})\|_\infty, \|V^{k-1}\|_\infty \}, \end{aligned}$$

then $\tau^{k+1} = \tau^k$. Else, $\tau^{k+1} = \alpha \tau^k$.

Step 4. Check convergence:

If

$$\frac{|f(x^k) - f(x^{k-1})|}{|f(x^{k-1})| + 1} \leq \text{tol}, \|g(x^k)_+\|_\infty \leq \text{tol}, \quad \text{and} \quad \|c(x^k)\|_\infty \leq \text{tol},$$

then stop.

Step 5. Set $k \leftarrow k + 1$ and go to Step 1.

In Step 0, we enter the initial data, to start our algorithm. In Step 1, we find an ϵ -global minimum, considering the multistart strategy. This technique is also considered in another augmented Lagrangian algorithm [19]. In Step 2, the inequality and equality constraint multipliers are updated, respectively. In Step 3, we measure the feasibility of the primal variable. If feasibility is assured, we keep parameter τ constant; otherwise, the parameter τ increases in value proportional to parameter α . In Step 4, we consider a stopping criterion for our algorithm. Note in Eq. (2.4) that

$$\lambda_i^{k+1} = \lambda_i^k h'(\lambda_i^k g_i(x^k) \tau^k) = \lambda_i^k \left(1 + \frac{\lambda_i^k g_i(x^k)}{\sqrt{(\lambda_i^k g_i(x^k))^2 + \frac{1}{(\tau^k)^2}}} \right), \quad i = 1, \dots, m.$$

2.2. Convergence

In this section, we present our main convergence result. It is known that second-order conditions on augmented Lagrangian functions can provide theoretical guarantees of assuming bounded penalty parameters; see, for example, the Proposition 1 of Bertsekas [5], Theorem 2.1 of Grapiglia and Yuan [20], and Proposition 4.2 of Cristofari et al. [13] and Conn et al. [11]. In our algorithm, we assume that the penalty parameter is bounded, because second-order conditions were already studied for the hyperbolic Lagrangian function by Ramirez et al. [31].

Theorem 2.1. *The sequences $\{x^k\}$, $\{\lambda^k\}$ and $\{\tau^k\}$ are generated by DHALA. The sequences $\{\tau^k\}$ and $\{\lambda^k\}$ are bounded. Suppose the whole sequence $\{x^k\}$ is convergent, i.e., $\lim_{k \rightarrow \infty} x^k = x^*$, then x^* is a feasible point.*

Proof. Let $x^k \in \Omega$ and we know that the set Ω is closed, then $x^* \in \Omega$. By hypothesis $\{\tau^k\}$ is bounded, then there exists k_0 such that $\forall k \geq k_0$, then the true condition in **Step 3** is verified. Thus, $\|c(x^k)\| \rightarrow 0$ and $g_i(x^k)_+ \rightarrow 0$, $i = 1, \dots, m$, that way we get a feasible point. On the other hand, we also have that $\|V^k\| \rightarrow 0$, then, we have $\|\lambda_i^k g_i(x^k)\| \rightarrow 0, \forall k \geq k_0$. ■

Theorem 2.2. *The sequences $\{x^k\}$, $\{\lambda^k\}$, $\{\mu^k\}$ and $\{\tau^k\}$ are generated by DHALA. Suppose that $\{\tau^k\}$, $\{\mu^k\}$ and $\{\lambda^k\}$ are bounded, and the whole sequence $\{x^k\}$ is convergent, i.e., $\lim_{k \rightarrow \infty} x^k = x^*$. Then x^* is an ϵ -global minimizer of the problem in Eq. (1.1).*

Proof. Let $\lim_{k \rightarrow \infty} x^k = x^*$ and by Theorem 2.1, we have that x^* is feasible. Let $y \in \Omega$, such that, $g_i(y) \leq 0, i = 1, \dots, m$, and $c_j(y) = 0, j = 1, \dots, p$. Since $\{\tau^k\}$ is bounded, we have $\tau^k = \tau^{k_0} = \bar{\tau} > 0, \forall k \geq k_0$. Now by the algorithm, we have

$$\begin{aligned} & f(x^k) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^k g_i(x^k) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(x^k) + \frac{\mu_j^k}{\bar{\tau}} \right)^2 \\ & \leq f(y) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^k g_i(y) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(y) + \frac{\mu_j^k}{\bar{\tau}} \right)^2 + \epsilon^k, \quad \forall k \geq k_0. \end{aligned} \quad (2.6)$$

Since $g_i(y) \leq 0, i = 1, \dots, m$, so we have that $\lambda_i^k g_i(y) \bar{\tau} \leq 0, i = 1, \dots, m, \forall k \geq k_0$, then by (P1) and (P2), we obtain

$$\frac{1}{\bar{\tau}} h(\lambda_i^k g_i(y) \bar{\tau}) \leq 0, \quad i = 1, \dots, m.$$

We apply this last in Eq. (2.6), thus

$$\begin{aligned} f(x^k) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^k g_i(x^k) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(x^k) + \frac{\mu_j^k}{\bar{\tau}} \right)^2 \\ \leq f(y) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(y) + \frac{\mu_j^k}{\bar{\tau}} \right)^2 + \epsilon^k. \end{aligned} \quad (2.7)$$

We know that $c_j(y) = 0, j = 1, \dots, p$, in Eq. (2.7), so we have

$$f(x^k) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^k g_i(x^k) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(x^k) + \frac{\mu_j^k}{\bar{\tau}} \right)^2 \leq f(y) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(\frac{\mu_j^k}{\bar{\tau}} \right)^2 + \epsilon^k. \quad (2.8)$$

On the other hand, there exists k_1 such that, for all $k \geq k_1 \geq k_0$ we have $\lim_{k \geq k_1} \lambda_i^k = \lambda_i^*, i = 1, \dots, m$ and $\lim_{k \geq k_1} \mu_j^k = \mu_j^*, j = 1, \dots, p$. Then from Eq. (2.8), and we apply limit, we have

$$f(x^*) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^* g_i(x^*) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(c_j(x^*) + \frac{\mu_j^*}{\bar{\tau}} \right)^2 \leq f(y) + \frac{\bar{\tau}}{2} \sum_{j=1}^p \left(\frac{\mu_j^*}{\bar{\tau}} \right)^2 + \epsilon, \quad (2.9)$$

since $c_j(x^*) = 0, j = 1, \dots, p$, by the inequality above, we have that

$$f(x^*) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^* g_i(x^*) \bar{\tau}) + \sum_{j=1}^p \frac{\bar{\tau}}{2} \left(\frac{\mu_j^*}{\bar{\tau}} \right)^2 \leq f(y) + \frac{\bar{\tau}}{2} \sum_{j=1}^p \left(\frac{\mu_j^*}{\bar{\tau}} \right)^2 + \epsilon. \quad (2.10)$$

It follows

$$f(x^*) + \frac{1}{\bar{\tau}} \sum_{i=1}^m h(\lambda_i^* g_i(x^*) \bar{\tau}) \leq f(y) + \epsilon. \quad (2.11)$$

From Theorem 2.1, we have $\lim_{k \geq k_1} \lambda_i^k g_i(x^k) = \lambda_i^* g_i(x^*) = 0, i = 1, \dots, m$, so from this, (P1) and by Eq. (2.11), we get

$$f(x^*) \leq f(y) + \epsilon, \quad (2.12)$$

thus, we obtain the desired proof. \blacksquare

2.3. Computational Experiments

All runs were conducted using an Intel Core i7-12700 (2.10 GHz) processor. For comparison purposes, we also implemented Algorithm 4.1 from Birgin and Martínez [8], but in Python, and we called this implementation QALA. To obtain a global solution to the subproblem generated by the augmented Lagrangian algorithm, we adopted a strategy similar to that considered by Gonçalves et al. [19], as follows: In Step 1 of algorithm DHALA, we use the L-BFGS-B algorithm, which is a local optimization algorithm. Then we run L-BFGS-B n -times using different randomly generated initial points (feasible with respect to the box Ω) and consider as the solution the point with the smallest value of the objective function of the subproblem, all of that is known as the multistart strategy.

With the algorithm QALA, we reproduce in Table 1 the values obtained in Table 2 of Birgin et al. [6]. In Table 1, we can observe that, our version of Algorithm 4.1 has the same objective function values reported by Birgin et al. [6] (for more details, see Section 5, Table 2 of Birgin et al. [6]), and achieves values very similar to the ALGENCAN algorithm (last column in Table 1).

In Table 1, in the column for our DHALA algorithm, we can see that the objective function values are very similar to those of the ALGENCAN algorithm. This shows that our proposed algorithm is competitive. In the same table, we also observe that the values obtained by DHALA algorithm are better than algorithms DF-EPGO [15] and HAL-iAFS [12], with respect to the value of the objective function.

Table 2 shows the parameters used by the DHALA and QALA algorithms to solve the 16 problems. The QALA parameters are the same as those suggested by Birgin et al. [6] for ALGENCAN.

Table 1: Optimal value of the objective function for the 16 problems of Birgin et al. [6]. Comparison between results obtained in this work and those of various authors [15, 12, 6]

Problem	DHALA	DF-EPGO [15]	HAL-iAFS [12]	QALA	ALGENCAN [6]
Problem 1	0.029249	0.06256	0.0342	0.029317	0.02930
Problem 2a	-399.999530	-134.09839	-380.674	-400.000081	-400.00000
Problem 2b	-600.004608	-705.13184	-385.051	-600.001301	-600.00000
Problem 2c	-750.000044	-82.95282	-743.416	-749.999996	-750.00000
Problem 2d	-399.999703	-399.76355	-399.492	-400.000478	-400.00000
Problem 3a	-0.388813	-0.38612	-0.3849	-0.385575	-0.38880
Problem 3b	-0.362113	-0.38881	-0.3888	-0.387574	-0.38880
Problem 4	-6.666667	-6.66665	-6.6667	-6.666667	-6.66660
Problem 5	201.159422	201.15915	201.159	201.159298	201.16000
Problem 6	376.291932	376.29266	376.292	376.291931	376.29190
Problem 7	-2.820042	-2.80585	-2.8284	-2.829680	-2.82840
Problem 8	-118.704859	-118.70476	-118.705	-118.707129	-118.70000
Problem 9	-13.402352	-13.40125	-13.4018	-13.401750	-13.40200
Problem 10	0.741782	0.74178	0.7418	0.742166	0.74170
Problem 11	-0.499983	-0.50000	-0.5000	-0.500088	-0.50000
Problem 12	-16.743059	-16.73887	-16.7389	-16.744445	-16.73900
Problem 13	189.346573	195.94547	189.345	189.346573	189.35000
Problem 14	-4.514385	-4.35233	-4.5142	-4.513896	-4.51420
Problem 15	0.000000	0.00000	0.0000	0.000000	0.00000
Problem 16	0.704924	0.71809	0.7049	0.704843	0.70500

Table 2: Parameters used by DHALA and QALA algorithms to solve the 16 problems in Birgin et al. [6]

Parameter	DHALA	QALA
λ_0	10.0	0.1
μ_0	0.1	0.1
τ_0	1.0	0.1
α	10.0	10.0
β	0.5	0.5
tol	10^{-2}	10^{-2}
Start points [†]	100	100

[†] The number of points of multistart L-BFGS-B.

3. Tangent Plane Distance Minimization for Phase Stability Analysis

The stability of thermodynamic phases plays a central role in chemical engineering applications, particularly in phase equilibrium calculations and process design. Assessing the *local stability* of a mixture involves determining whether the system lies at a local minimum of the Gibbs free energy surface. A powerful tool for this purpose is the *Tangent Plane Distance (TPD)* criterion, originally developed by Michelsen [22], which reformulates the stability problem as an optimization problem over the composition space. Formally, for a given mixture with c components at feed composition \mathbf{z} , temperature T , and pressure P , the system is stable with respect to phase splitting if and only if the Gibbs energy tangent plane at \mathbf{z} lies below the molar Gibbs energy surface at all other compositions \mathbf{x} . The TPD function is defined as:

$$\text{TPD}(\mathbf{x}; \mathbf{z}) = \xi G(\mathbf{x}) - \xi G(\mathbf{z}) - \nabla(\xi G(\mathbf{z})) \cdot (\mathbf{x} - \mathbf{z}) , \quad (3.13)$$

where

$$\xi G(\mathbf{x}) = \sum_{i=1}^c x_i \ln x_i + \xi G^E(\mathbf{x}) \quad (3.14)$$

and G^E denotes the molar excess Gibbs energy and $\xi RT = 1$, being R the universal gas constant and T the absolute temperature. The TPD function measures the distance between the tangent plane at \mathbf{z} and the excess Gibbs energy at a trial composition \mathbf{x} . A negative TPD value indicates that a composition \mathbf{x} exists with lower Gibbs energy than predicted by the tangent plane at \mathbf{z} , signaling phase instability and potential phase separation. The minimization of the TPD function over all admissible compositions (typically the mole fraction) allows one to assess local stability:

$$\begin{aligned} & \min_{\mathbf{x} \in \mathbb{R}^c} \text{TPD}(\mathbf{x}; \mathbf{z}) , \quad \text{subject to} \\ & 1 - \sum_{i=1}^c x_i = 0 , \\ & 0 \leq x_i \leq 1 , \quad \forall i = 1, 2, \dots, c . \end{aligned}$$

If the global minimum of the TPD function is non-negative, the system is locally stable. Otherwise, the system is unstable and prone to phase separation. In this work, we focus on liquid–liquid systems, where the non-ideal

(SF):

$$\begin{aligned}
 \min_{\mathbf{x} \in \mathbb{R}^c} \sum_{i=1}^n \left[x_i \left(\ln \left(\frac{x_i}{z_i} \right) - \ln \gamma_i(\mathbf{z}) \right) \right] + \xi G^E(\mathbf{x}) \quad , \quad \text{subject to} \\
 \text{SF :} \quad \quad \quad -1 + \sum_{i=1}^c x_i - \varepsilon \leq 0 \quad , \\
 \quad \quad \quad \quad \quad 1 - \sum_{i=1}^c x_i - \varepsilon \leq 0 \quad , \\
 \quad \quad \quad \quad \quad 0 \leq x_i \leq 1 \quad , \quad \forall i = 1, 2, \dots, c \quad ,
 \end{aligned}$$

where $0 < \varepsilon \ll 1$. In the following results, we set $\varepsilon = 10^{-8}$. Those formulations emphasizes the *global optimization* nature of the problem: due to the nonconvexity of the function $\xi G^E(\mathbf{x})$, local minima may exist that do not correspond to the global one. Therefore, global optimization techniques become essential for correctly assessing stability.

In our work, we use TPD minimization as a case study to illustrate the application of global optimization algorithm proposed. The high nonlinearity and multimodal character of the TPD objective function under NRTL make it a challenging benchmark for global solvers. Gecegormez and Demirel [18] investigated phase stability analysis by combining the tangent plane distance (TPD) criterion with the NRTL activity coefficient model, and solved the resulting highly nonlinear system using the interval Newton method. The interval Newton method, a generalized bisection algorithm with interval arithmetic, was shown to be more robust and capable of locating all stationary points—including minima, maxima, and saddle points—within the composition domain, thus ensuring a reliable detection of phase instability. The authors tested the methodology on ten binary and two ternary liquid systems, many of them strongly non-ideal polar mixtures (see Table 3) with several different feed compositions, totaling 140 TPD minimization problems, and successfully identified multiple stationary points of the TPD function.

Table 3: Identification of the systems analyzed by Gecegormez and Demirel [18] highlighting their chemical components, temperature, and pressure. The systems whose results will be presented and discussed in more detail throughout this section are highlighted in bold. The results of the others are in the Supplementary Information

ID	System
1	n-pentanol(1) + 2,2-dimethylbutane(2) at 25°C and 1 atm
2	n-pentanol(1) + 2-methylpentane(2) at 25°C and 1 atm
3	ethanol(1) + cyclohexane(2) at 5°C and 1 atm
4	water(1) + butyl glycol(2) at 5°C and 1 atm
5	water(1) + citric acid(2) at 25°C and 1 atm
6	citric acid(1) + 1-butanol(2) at 25°C and 1 atm
7	citric acid(1) + 2-butanol(2) at 25°C and 1 atm
8	water(1) + 1,4-dicyanobutane(2) at 25°C and 1 atm
9	water(1) + butanenitrile(2) at 25°C and 1 atm
10	water(1) + benzonitrile(2) at 25°C and 1 atm
11	acetonitrile(1) + benzene(2) + n-heptane(3) at 45°C and 1 atm
12	water(1) + citric acid(2) + 2-butanol(3) at 25°C and 1 atm

We applied our global algorithm to solve all the problems analyzed by Gecegormez and Demirel [18], whose NRTL parameters \mathcal{G}_{ji} and τ_{ji} and feed compositions were provided by the authors. The algorithm parameters used for all runs are shown in Table 4.

Table 4: Parameters used by DHALA and QALA in the TPD minimization examples

Parameter	DHALA	QALA
λ_0	100.0	100.0
μ_0	0.1	0.1
τ_0	2.0	2.0
α	10.0	10.0
β	0.5	0.5
tol	10^{-8}	10^{-8}
Start points [†]	150	150

[†] The number of points of multistart L-BFGS-B.

Among the 140 cases analyzed in this work, 133 presented the same solution reported by Gecegormez and Demirel [18]. In the other 7 cases, a

solution with a lower TPD value than that reported by these authors was obtained. Therefore, this section will focus in more detail on these 7 examples, while the others can be seen in the Supplementary Information. The results of these 7 problems are reported in Table 5, where one can find the optimal value of TPD reported by Gecegormez and Demirel [18] and the values obtained with DHALA and QALA for the two formulations presented: original (OF, with equality constraints) and splitted (SF, with inequality constraints). The execution time, in seconds, of the algorithms is also indicated. As can be seen in Table 5, DHALA and QALA overcome the authors' solutions in all 7 problems.

Table 5: 7 Problems of Gecegormez and Demirel [18]

ID	z	Lit. [18]	TPD($x^*; z$)			Time in seconds		
			DHALA		QALA	DHALA		QALA
			split	split	original	split	split	original
11	[0.40, 0.05, 0.55]	-0.005 225	-0.108 458	-0.108 458	-0.108 458	5.4833	5.8086	6.9720
11	[0.45, 0.05, 0.50]	-0.015 280	-0.086 610	-0.086 610	-0.086 610	5.3527	6.6757	7.4836
11	[0.50, 0.10, 0.40]	-0.028 673	-0.039 224	-0.039 224	-0.039 224	5.4072	5.4035	5.2335
11	[0.45, 0.15, 0.40]	-0.011 712	-0.034 601	-0.034 601	-0.034 601	4.2583	5.2599	5.7719
11	[0.45, 0.20, 0.35]	-0.008 643	-0.016 034	-0.016 034	-0.016 034	4.1603	4.2630	5.9169
12	[0.10, 0.05, 0.85]	-0.004 448	-0.160 857	-0.160 857	-0.160 857	3.0665	3.3167	3.3921
12	[0.05, 0.10, 0.85]	-0.047 370	-0.140 854	-0.140 854	-0.140 854	3.9812	4.2037	4.4752

In order to demonstrate that these are not merely more refined solutions than those proposed by Gecegormez and Demirel [18], Figures 1 and 2 show that the position of the solution in the composition plane changes radically in the systems of acetonitrile(1) + benzene(2) + n-heptane(3) and water(1) + citric acid(2) + 2-butanol(3), respectively. In these diagrams, the horizontal axis represents the molar fraction of component 1, while the vertical axis represents the molar fraction of component 2. The molar fraction of component 3 is not linearly independent from the others, since $x_1 + x_2 + x_3 = 1$. The color scale represents the TPD value. The green squares indicate the composition of the feed phase, while the blue dot and yellow cross indicate the solutions obtained in this work and by Gecegormez and Demirel [18], respectively.

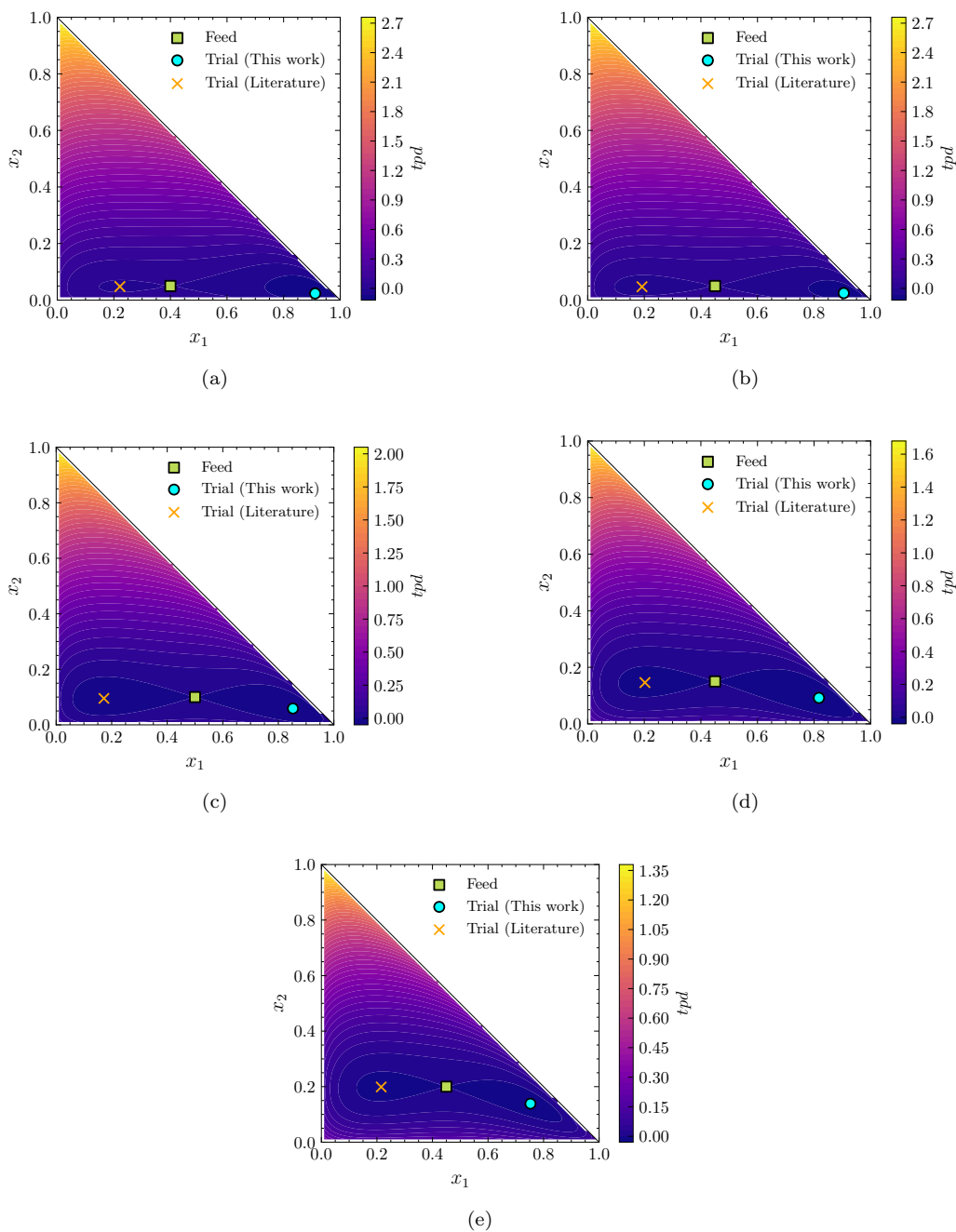


Figure 1: Tangent Plane Distance function for the acetonitrile(1) + benzene(2) + n-heptane(3) system at 45 °C and 1 atm with various different feed compositions (see Table 5): (a); (b); (c); (d); (e). Green squares represent the position of the feed compositions; blue circles represent the optimal test compositions obtained in this work; and yellow crosses represent the test compositions reported by Gecegormez and Demirel [18].

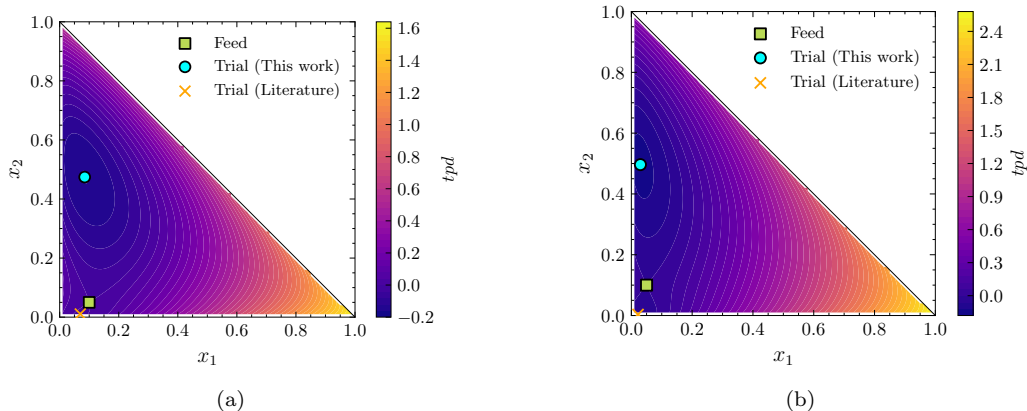


Figure 2: Tangent Plane Distance function for the water(1) + citric acid(2) + 2-butanol(3) at 25 °C and 1 atm with various different feed compositions (see Table 5): (a); (b); (c); (d); (e). Green squares represent the position of the feed compositions; blue circles represent the optimal test compositions obtained in this work; and yellow crosses represent the test compositions reported by Gecegormez and Demirel [18].

Regarding the performance comparison of the two algorithms, in all 140 problems, DHALA and QALA obtained the same solutions in both formulations. However, DHALA required less time to run the 140 problems than QALA, as show in Table 7. Therefore, we conclude that our proposed algorithm is competitive and superior in runtime to safeguards techniques for this particular type of problem, which is found in the area of chemical engineering.

Table 7: Total time (in seconds) to solve all 140 problems with DHALA and QALA for the two formulations presented (OF and SP)

Parameter	Original Formulation	Split Formulation
DHALA	-	468
QALA	566	508

4. Conclusions

To our knowledge, this work is among the first to investigate augmented Lagrangian methods on a large benchmark of 140 TPD instances. We study two augmented Lagrangian algorithms: QALA and DHALA. Table 1 show that DHALA is computationally compatible with other algorithms known in the literature, achieving objective function values comparable to those reported by other algorithms. Moreover, Tables 5 and 7 indicate that both

QALA and DHALA attain better objective function values than the approach of Gecegormez and Demirel [18], which does not use augmented Lagrangian techniques. These results also show that DHALA solves the 140 instances faster than QALA. This computational evidence motivates further investigation of augmented Lagrangian methodologies for the TPD problem.

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