Global Optimization Algorithms to Compute Thermodynamic Equilibria in Large Complex Systems with Performance Considerations

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Abstract

Several global optimization methods are reviewed that attempt to ensure that the integral Gibbs energy of a closed isothermal isobaric system is a global minimum to satisfy the necessary and sufficient conditions for thermodynamic equilibrium. In particular, the integral Gibbs energy function of a multi-component system containing non-ideal phases may be highly non-linear and non-convex, which makes finding a global minimum a challenge. Consequently, a poor numerical approach may lead one to the false belief of equilibrium. Furthermore, confirming that one reaches a global minimum and that this is achieved with satisfactory computational performance becomes increasingly more challenging in systems containing many chemical elements and a correspondingly large number of species and phases. Several numerical methods that have been used for this specific purpose are reviewed with a benchmark study of three of the more promising methods using five case studies of varying complexity. A modification of the conventional Branch and Bound method is presented that is well suited to a wide array of thermodynamic applications, including complex phases with many constituents and sublattices, and ionic phases that must adhere to charge neutrality constraints. Also, a novel method is presented that efficiently solves the system of linear equations that exploits the unique structure of the Hessian matrix, which reduces the calculation from a $O(N^3)$ operation to a $O(N)$ operation. This combined approach demonstrates efficiency, reliability and capabilities that are favorable for integration of thermodynamic computations into multi-physics codes with inherent performance considerations.

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8 9 **1. Introduction**

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11 Computational thermodynamics plays an integral role in facilitating engineering design of a wide array of
12 materials and processes. Many equilibrium solvers have been developed to assist in this process, which rely
13 on numerical methods and algorithms to compute thermodynamic equilibria. Upon initial impression, the
14 number of publications in the open literature pertaining to this subject matter appears rather exhaustive.
15 However, the majority of articles describing global optimization methods applied to computational thermo-
16 dynamics deal with relatively small systems, such as liquid-vapor equilibria, or are aimed at solving only a
17 handful of calculations [1, 2, 3, 4, 5, 6, 7]. Although these methods work well for relatively small systems
18 or when only a few calculations are needed, they were not developed to handle very large systems or for
19 integration of thermodynamic calculations into multi-physics codes, which puts much greater demands on
20 reliability and efficiency. This has been the impetus of developing THERMOCHIMICA [8] for integration into
21 multi-physics codes, such as the BISON [9] nuclear fuel performance code. The goal of this paper is to review
22 some of the more promising algorithms with greater mathematical rigor and to focus on performance issues
23 that become more prominent as the size and complexity of thermodynamic systems increases.
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34 The computation of thermodynamic equilibria rests on the minimization of the integral Gibbs energy
35 of a closed isothermal-isobaric system subject to linear equality and inequality constraints represented by
36 conservation of mass and the Gibbs phase rule. The Gibbs energy function of non-ideal phases may be
37 non-convex, yielding multiple local minima. Local minima correspond to different compositions of phases
38 that may be believed to be stable (e.g., a miscibility gap), which may not necessarily correspond to the
39 true equilibrium composition. Finding the global minimum of this function among the many local minima
40 within the domain space can be a daunting challenge, especially in large complex thermodynamic systems
41 containing many highly non-ideal solution phases. Consequently, an inadequate numerical approach may
42 lead one to the false belief of thermodynamic equilibrium, which may be far from the true equilibrium state.
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50 There are several significant issues with finding a global minimum of the integral Gibbs energy function.
51 First, *no global optimization technique guarantees the ability of finding a global extremum of a nonconvex*
52 *function* [10]. One can, however, gain a certain level of confidence in applying a particular algorithm to
53 a specific type of problem within a well defined perimeter of application. Second, searching for a global
54 minimum becomes increasingly more difficult as the size of the system increases. And finally, the computa-
55 tional effort associated with performing this task can increase very rapidly in large systems, which can be
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a significant obstacle to integrating thermodynamic computations into multi-physics codes. The necessary and sufficient conditions for thermodynamic equilibrium at constant temperature and pressure are reviewed in §2 and several global optimization techniques that have been applied to the thermodynamic equilibrium problem are reviewed in §3. Three particular methods that have been found effective in computational thermodynamics are further examined in five case studies of varying complexity in §4. Finally, the behaviour and suitability of these methods are discussed in §5.

2. Necessary and Sufficient Conditions for Thermodynamic Equilibrium at Constant Temperature and Pressure

The necessary conditions for thermodynamic equilibrium require satisfaction of mass conservation and Gibbs' phase rule. The sufficient condition for equilibrium in a closed system at constant temperature and pressure corresponds to a global minimum of the integral Gibbs energy function. Ensuring that the mass balance constraints and the Gibbs phase rule have been satisfied is straightforward; however, special attention must be given to confirming that the Gibbs energy of a system, G , is at a global minimum³. For sake of completeness, the necessary conditions are briefly reviewed while the manuscript as a whole is dedicated to the sufficient condition of equilibrium.

First, the mass balance constraints must be satisfied. The total mass of system component j is represented by b_j and is computed by

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} a_{i(\lambda),j} + \sum_{\omega=1}^{\Omega} n_{\omega} a_{\omega,j} \quad (1)$$

where N_{λ} denotes the number of species in solution phase λ , and Λ and Ω represent the total number of stable solution phases and pure condensed phases in the system. The mole fraction of species i in solution phase λ is represented by $x_{i(\lambda)}$, and n_{λ} and n_{ω} represent the total number of moles of solution phase λ and pure condensed phase ω , respectively. The stoichiometry coefficients of component j in species i and pure condensed phase ω are $a_{i(\lambda),j}$ and $a_{\omega,j}$ (g-at·mol⁻¹), accordingly. Clearly, n_{λ} and n_{ω} must be non-negative and $0 < x_{i(\lambda)} < 1$.

A solution phase may be represented as a multi-sublattice model, whereby the species are represented by a fixed combination of constituents that contain only a single constituent on each sublattice. Thus, constituents

³Of course, thermodynamic equilibrium can be calculated for other conditions, such as fixed enthalpy or chemical potential of a component. The conditions described herein exclusively pertain to a closed system at constant temperature and pressure.

are a subset of the species. Furthermore, the species may then be interpreted as stoichiometric compounds representing the extremes of composition and are commonly referred to as “compound end members”. The mole fraction of species i , or compound end member, is related to the site fractions of constituents, $y_{i(s)}$, on all sublattices in the phase corresponding to i through the following formalism

$$x_{i(\lambda)} = \prod_{s=1}^{N_s} y_{i(s)} \quad (2)$$

where s is the sublattice index and N_s is the number of sublattices.

Second, the equilibrium condition must also abide Gibbs’ phase rule, which requires that the number of thermodynamic degrees of freedom, F , be non-negative. For a closed isothermal-isobaric system, F is defined as the difference between the number of system components, C , and the total number of stable phases, Φ (i.e., $\Phi = \Lambda + \Omega$) as

$$F = C - \Phi \quad (3)$$

where maintaining constant temperature and pressure removes two degrees of freedom. Thus, Gibbs’ phase rule requires that the number of co-existing phases at equilibrium in an isothermal isobaric closed system must be less than or equal to the number of system components (i.e., $1 \leq \Phi \leq C$). A system component is the most basic form of representing part of a thermodynamic system, which is often taken as a chemical element or by a fixed integer combination of chemical elements. The term “system component” is used here to distinguish from a “phase component”, which typically represents a species in a solution phase.

Finally, the sufficient condition for equilibrium requires that G is at a global minimum with respect to the quantities of all species and phases. The integral Gibbs energy of a multicomponent multiphase system can be represented as

$$G = \sum_{\lambda=1}^{\Lambda} n_{\lambda} g_{\lambda} + \sum_{\omega=1}^{\Omega} n_{\omega} g_{\omega} \quad (4)$$

where g_{λ} and g_{ω} are the molar Gibbs energies of solution phase λ and pure condensed phase ω , respectively. The latter is fixed, whereas the formulation of g_{λ} is model dependent and is a non-linear function of $x_{i(\lambda)}$. This term is responsible for the non-convexity of G .

A local minima⁴ in G , which may differ from the global minimum, is indicated by $dG = 0$. An equivalent

⁴Numerical methods that locally minimize G subject to mass balance constraints have been extensively documented in the literature [8, 11, 12, 13] and are not discussed herein.

statement yields the following linear equality⁵ [14, 15]

$$\mu_i = \sum_{j=1}^C a_{i,j} \Gamma_j \quad (5)$$

where μ_i is the chemical potential of species i and Γ_j is the chemical potential of system component j . Equation (5) states that the chemical potential for each system component must have the same value in all stable phases within the system [15]. This equation is often graphically represented as a tangent line between phases on a molar Gibbs energy plot in a binary system or equivalently as a hyperplane in higher order systems. This is sometimes called the ‘‘Gibbs plane’’, whereby the corners of the Gibbs plane are given by Γ_j and any point on this plane is μ_i .

The linear equality represented by equation (5) is used to justify the selection of stable phases and ensuring that no metastable phase should be added to the system. The molar Gibbs energy of any metastable solution phase λ must be greater than the corresponding value computed by the chemical potentials of the system components at equilibrium. An equivalent statement is that the lowest point of a phase that is believed to be metastable should be above the Gibbs plane, which would be the lowest common tangent plane at equilibrium. The difference between the Gibbs plane and the plane tangent to a metastable phase is often referred to as the ‘‘driving force’’ [16] or ‘‘tangent plane distance function’’ [16, 17], which is represented for solution phase λ as π_λ and is computed by

$$\pi_\lambda = \min_x \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j \right) \quad (6)$$

which is subject to the following linear equality and inequality constraints

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1, \quad x_{i(\lambda)} > 0, \quad \forall i \quad (7)$$

Some representations of the driving force represent the negative value of π_λ instead [18]. Note that equation (6) is independent of the type of thermodynamic model corresponding to λ , which equally applies, for example, to regular substitutional models or multi-sublattice models. Ionic phases – such as an aqueous phase, plasma or ionic solid solutions – must also adhere to charge neutrality, given by

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} a_{i,j} = 0, \quad (8)$$

⁵A thorough derivation and discussion of this necessary condition is provided by Piro *et al* [14].

where $a_{i,j}$ denotes the net ionic charge of species i in solution phase λ . Recall that the electron is treated as a system component in an ionic phase (i.e., $j = e^-$).

Mathematically speaking, the linear equality given by equation (5) represents a local minima in the integral Gibbs energy function, which may not necessarily correspond to the true equilibrium condition. Satisfaction of this equation will be referred to henceforth as a “local equilibrium” involving a specific assemblage of phases believed to be stable to differentiate the term from a “local minima” on the π_λ surface of metastable phases.

Therefore, the necessary conditions for equilibrium must satisfy equations (1), (3) and (5), and the sufficient condition requires that π_λ computed with equation (6) is non-negative for all phases believed to be metastable. As demonstrated by Hillert [15], one can compute π_λ for all metastable phases throughout the iterative process to determine whether a particular solution phase should be added to the system. This function can be nonconvex and must be given careful consideration to determine whether π_λ is at a global minimum rather than at a local minima. The following section reviews several approaches that have been taken in handling this issue.

3. Brief Review of Global Optimization Methods

Global optimization methods are generally categorized as deterministic or stochastic. Numerous methods that fall within these categories have been used in a wide variety of applications and their success is always problem-specific. For the case of computational thermodynamics, the driving force is bounded by $x_{i(\lambda)} \in (0, 1)$ and the dimension of the domain space is defined by the number of species in that particular solution phase, thus $x_{i(\lambda)} \in \mathbb{R}^{N_\lambda}$. Fortunately, π_λ generally does not have many local minima, it is smooth and it does not have deep narrow valleys, which plague other global optimization problems outside of the field of computational thermodynamics [19].

The utility of any method must be realized within the perimeter of its intended application. For instance, the algorithmic requirements for systems involving vapor-liquid equilibria is not as demanding as that of a general solver intended to handle systems exceeding 40 chemical elements, such as irradiated nuclear fuel [20]. The computational demands are much more significant in integration of thermodynamic computations in multi-physics codes with very frequent execution, especially when involving large thermodynamic systems. Ideally, a numerical method should be reliable, computationally efficient, independent of any particular type of thermodynamic model and is equally applicable to solution phases with any number of species.

Although there are many global optimization methods that have been implemented in thermodynamic solvers, which are broadly reviewed by Zhang *et al* [17], the ensuing discussion focuses specifically on the computational difficulties that are more pronounced in large complex systems and when thermodynamic computations are integrated in multi-physics codes. Furthermore, only a handful of commonly used methods are described to permit a more detailed discussion of the numerical performance and robustness in §4.

3.1. Stochastic Methods

Stochastic optimization methods incorporate randomness in the minimization (or maximization) of an objective function. These methods generally rely on a two step process whereby the first step explores the domain space while the second step relies on the intensification of the search for an optimum solution. Heuristic or analytical learning strategies are often used to expedite the process. Several commonly used stochastic methods that have been applied to computational thermodynamics include Simulated Annealing [21], Particle Swarm Optimization (PSO) [3], Tabu search [6], Genetic Algorithm [22], Ant Colony Optimization [23], Cuckoo search [4] and Random Tunnelling Algorithms [24]. Of all of the aforementioned stochastic methods, the authors have found that the PSO method offers the best combination of reliability, flexibility and efficiency in the context of thermodynamic equilibrium computations, and is therefore selected in the benchmark analysis in §4.

3.1.1. Particle Swarm Optimization

PSO is a stochastic method inspired by swarm like behaviour in the animal kingdom, such as the migration of a swarm of bees [25]. In this method, a “swarm” of particles representing individual candidate solutions in the feasible region are initially generated, either at random or at pre-determined locations, which are then permitted to traverse the search space. The movement of each particle is influenced by both its best known local and global positions, which are both adjusted as the swarm traverses the search space with the hope of migrating to a global optimum.

The position vector of each particle, $\mathbf{x}_p^m$, at iteration m is altered based on a computed velocity vector, $\mathbf{v}_p^m$, by

$$\mathbf{v}_p^m = \psi \mathbf{v}_p^{m-1} + \phi_p r_p (\mathbf{x}_p^* - \mathbf{x}_p^m) + \phi_s r_s (\mathbf{x}_s^* - \mathbf{x}_p^m) \quad (9)$$

where $\mathbf{x}_p^*$ and $\mathbf{x}_s^*$ are the position vectors of the best known local minima near particle p and the best known global minimum of the entire swarm, respectively. One may interpret the first term in equation (9) as the inertia of particle p , the second term attracts p to its nearest best estimate and the third term propels p to

the best estimate of the swarm. The terms ψ , ϕ_p and ϕ_s are tunable parameters that are problem specific, which have direct influence on the behaviour and efficacy of the overall method. Finally, $r_p \in (0, 1)$ and $r_s \in (0, 1)$ are randomly generated numbers that influence the tendency of a particle towards the best local minima or the global minimum of the swarm. The position vector of particle p is updated via the following equation

$$\mathbf{x}_p^{m+1} = \mathbf{x}_p^m + \mathbf{v}_p^m \quad (10)$$

The authors have found that an effective strategy for PSO for finding the global minimum of π_λ is to have N_λ particles in the swarm, which are initially released at the N_λ corners of the domain space. The position of each particle is updated with equation (10), whereby the velocity vector represented by equation (9) is scaled at each iteration to prevent $x_{i(\lambda)}$ from escaping the feasible region (i.e., $0 < x_{i(\lambda)} < 1$). The stopping criteria may include a number of factors, such as the convergence of all particles in the swarm to a minimum within a specific tolerance, a maximum number of iterations or a negative value of π_λ .

The authors have found that values for $\psi = 0.5$, $\phi_p = 2$ and $\phi_s = 2$ provide good convergence rates while also sufficiently sweeping the search space. Relatively large values for ϕ ensure reasonable intensification when the swarm approaches a global minimum; however, the maximum increment in $x_{i(\lambda)}$ of any particle is constrained to prevent any local valleys from being missed. The tunable parameter ψ can also be varied to shift emphasis of a particle's trajectory from a global search to a local search. The authors have found that a more effective method of tuning PSO to thermodynamic equilibrium problems is to progressively relax the constraints imposed on the velocity magnitude via the following equation

$$\|\mathbf{v}\| \leq v_{min} + \frac{v_{max} - v_{min}}{m_{max} - 1}(m - 1) \quad (11)$$

where v_{max} and v_{min} are prespecified maximum and minimum velocity magnitudes respectively, and m_{max} is the maximum number of iterations permitted in PSO. Thus, the optimization begins with a fairly local neighborhood, which gradually increases in size as the iteration cycle progresses.

3.2. Deterministic Methods

The foundation of deterministic methods is to analytically capture the behaviour of a system in a logical manner. These methods rely on a local minimizer of π_λ subject to linear equality and inequality constraints, which may employ steepest descent, Newton or quasi-Newton methods. Derivations of the Lagrangian function of π_λ and the Hessian matrix are given in Appendix A. The resulting Hessian yields a symmetric arrow matrix, which can be solved very efficiently using a method presented in Appendix B that exploits

the unique structure of this matrix, which reduces the solution of the system of linear equations from an $O(N^3)$ to an $O(N)$ operation. This procedure alone alleviates a major performance concern that is often encountered in ensuring a global minimum in the Gibbs energy function using deterministic methods.

Deterministic methods that have been applied to thermodynamic equilibrium computations include the grid construction, Terminal Repeller Unconstrained Subenergy Tunneling (TRUST) [26], and Branch and Bound (B&B) [27] methods. The grid construction method has been used in a number of thermodynamic codes and will be included in the discussion. The authors have found the B&B method to be the most effective among the foregoing deterministic optimization methods applied to thermodynamic equilibrium problems, which will be further explored in §3.2.2.

3.2.1. Grid Construction

A strategy for testing stable equilibria that has been adopted by many thermodynamic codes is to perform numerous function evaluations of π_λ at regular intervals in the domain space [5, 13, 18, 28, 29]. The foundation of this approach is to discretize the surface of π_λ into a grid, whereby each grid point corresponds to a unique composition of that phase. Thus, one can interpret each grid point as being a stoichiometric compound and the ensemble of these grid points collectively approximate the driving force surface.

Figure 1 illustrates the concept of grid construction for an arbitrary A-B binary system comprised of solution phase α and pure stoichiometric phase A_3B_2 . The dotted line tangent to the α phase connecting A_3B_2 represent the predicted state of equilibrium at a particular iteration. In this approach, the domain for solution phase α is in N_α dimensional space, where each dimension corresponds to each species in that phase. For this example, solution phase α is comprised of species A_α and B_α (i.e., $N_\alpha = 2$). Note that although π_α is used in the evaluation, the molar Gibbs energy function is plotted in Figure 1 for convenient and familiar illustration purposes. The size of the domain is defined by the number of solution phase species, not the system components. Since the solution phase species (i.e., A_α and B_α) correspond directly to the system components (i.e., A and B) for this example, they are plotted for sake of convenience.

For the specific implementation of the grid method shown in Figure 1, a grid point is placed near the extremes (i.e., $\chi_B = 0.01$ and $\chi_B = 0.99$) with other points evenly distributed. In Figure 1, the intermediate points have an equal spacing of 0.1 yielding a total of 11 grid points. As demonstrated by Chen *et al* [29], one must be very careful to sufficiently discretize the domain space to avoid missing critical features of the molar Gibbs energy surface. For example, the composition interval in Figure 1 is too large and the local minima of π_α that resides between α_1 and α_2 is not recognized. Consequently, one would be under the false impression of stable equilibria for this particular problem.

Figure 1: The molar Gibbs energy surface for an arbitrary solution phase α is partitioned into 11 grid points in the grid method (represented by hollow circles at $x_B = 0.01, 0.1, 0.2, \dots, 0.9, 0.99$) for a binary closed system at constant temperature and pressure. The pure stoichiometric phase A_3B_2 and solution phase α are predicted to be stable (as represented by the dashed tangent line); however, they are in fact metastable and an $\alpha - \alpha$ miscibility would yield a lower value of G .

The critical feature of the molar Gibbs energy curve in the example system shown in Figure 1 between α_1 and α_2 can be identified with a higher resolution grid. Extending this approach to higher order systems is not clearly explained in the literature. A concern is that if one maintains the same level of resolution that the number of function evaluations can be very large, which would lead to computational performance concerns.

Suppose one attempted to find the global minimum of the molar Gibbs energy surface (or driving force) by constructing a grid in N_λ dimensional Euclidean space and each dimension corresponds to a particular species in that phase. Let δ represent a constant grid spacing (i.e., the increment in the mole fraction), ϵ the number of variations, or equivalently, the reciprocal of the increment (i.e., $\epsilon = 1/\delta$, where $\delta \in \mathbb{R}$ and $\epsilon \in \mathbb{Z}$) and ζ is the total number of grid points for a particular solution phase. Additional grid points are constructed in the vicinity of each pure species in a similar fashion as Figure 1. Therefore, the total number of unique grid points in N_λ dimensional space is,

$$\zeta = \frac{(\epsilon - 1)!}{(\epsilon - N_\lambda)!(N_\lambda - 1)!} + N_\lambda \quad (12)$$

Given that ζ is a function involving multiple factorials, the number of grid points can be extremely large for even a modest number of species when using this specific implementation of the grid method. Table

1 gives a few arbitrary example scenarios varying the number of species and the grid spacing to give an impression of the number of grid points required for this approach. Of course, this equation applies to a specific implementation of the concept of grid construction, which may vary depending on its implementation in different software. For example, Chen *et al* [28] use 8 evenly distributed grid points in a binary phase, which would fail in finding the local minima in Figure 1 near $\chi_B = 0.05$. The open-source code OpenCalphad [18] also uses the grid construction method, whereby 8 grid points are constructed for a solution phase with two species and two of the grid points are located very near the extremums (i.e., similar to Figure 1). It is unable to find the global minimum with 8 grid points, but it also has an option for the user to select a denser grid that yields 28 points, which is able to find the minimum. It is not clear how the method from Chen *et al* [28] or Sundman *et al* [18] extend their respective approaches to higher order phases.

Table 1: The number of grid points, ζ , required to represent N_λ species in a solution phase with δ resolution is tabulated below for several arbitrary scenarios. The first row corresponds to the example system given in Figure 1.

N_λ	δ	ϵ	ζ
2	0.1	10	11
2	0.05	20	21
5	0.05	20	3,881
5	0.01	100	3,764,381
10	0.01	100	1.73×10^{12}
20	0.01	100	1.07×10^{20}

As is evident in Table 1, the number of grid points generated with this procedure increases very rapidly with higher dimensional phases, which can significantly affect computational performance as a result of an extremely large number of function evaluations. Furthermore, a global minimum may not necessarily be found even when near a computed grid point with a high resolution grid. Of course, the number of grid points that are used depends on the manner that this general approach is implemented into the programming.

3.2.2. Branch and Bound

The Branch and Bound (B&B) algorithm [27] involves two procedures to solve global optimization problems. The first partitions the feasible domain D into two or more smaller disjoint subdomains $D_1, D_2, \dots$, whose union covers the entire domain D . This procedure is commonly referred to as “branching” since it bears resemblance to the structure of a tree branch and may be repeated recursively. The second procedure referred to as “bounding” computes the upper and lower bounds of the objective function within a subset

of the feasible space D . The classical B&B method is based on the principle that a subdomain may be removed from the analysis (i.e., “pruning”) if its lower bound is greater than the upper bound for any other subdomain. Therefore, the partitioned objective function is considered convex within each subdomain D_i as a model of the true nonconvex objective function that spans the entire domain D .

Conventionally, the B&B method is applied to mixed integer linear programming problems [30], but the fundamental concepts can be applied to continuous nonconvex real functions. This type of approach has been applied by McDonald and Floudas [1] to solve thermochemical equilibria. A modified version of the conventional B&B method was implemented in the thermodynamic equilibrium software library THERMOCHIMICA [8] that performs a different initialization procedure and relaxation scheme of the upper and lower bounds and is presented herein. Furthermore, all of the subdomains are evaluated until an appropriate stopping criterion has been satisfied, unlike the traditional B&B method that relies heavily on “pruning” techniques. Finally, an active recursive partitioning technique of the subdomains is performed if determined necessary.

The approach taken by THERMOCHIMICA partitions the domain D for a particular solution phase λ into N_λ subdomains and the driving force π_λ is minimized within each subdomain. The derivation of the Lagrangian function that minimizes π_λ is given in Appendix A. One can interpret each subdomain D_i as a region in domain D with a relatively high concentration of the i th species. Unlike the conventional B&B technique, the bounds of each subdomain are relaxed while the bounds of the domain (i.e., $0 < x_{i(\lambda)} < 1$) are strictly enforced to avoid numerical instabilities. Specifically, the upper and lower bounds of the subdomain D_i are $\mathcal{U}_i < 1$, $\mathcal{L}_i = 0.5$, $\mathcal{U}_{j \neq i} < 0.5$ and $\mathcal{L}_{j \neq i} > 0$. Each subsystem is initialized at the corners of the respective subdomain D_i by $x_i = [1 - 0.001 \times (N_\lambda - 1)]$ and $x_{j \neq i} = 0.001$. The stopping criteria within each subdomain is reached if the local minimizer leaves the perimeter of the respective subdomain or if a local minima is found. In the event that there are multiple local minima, a successive refinement technique is pursued that constructs additional subdomains whereby the upper and lower bounds of the subdomain are defined by the two local minima and the minimization procedure is initiated in the middle of the respective subdomain.

The arbitrary binary system from Figure 1 is reconsidered in Figure 2 using the modified branch and bound technique. As in the previous example, solution phase α and pure stoichiometric phase A_3B_2 are initially predicted to be stable. To ensure that the system is in thermodynamic equilibrium, the domain representing solution phase α is partitioned into two subdomains in Figure 2 (since there are two species in solution phase α). The minimization of π_α within each subdomain is initialized at the corners of the domain, as indicated in Figure 2 (again, the molar Gibbs energy function is plotted instead of π_λ for sake of

Figure 2: The arbitrary binary system given in Figure 1 is reconsidered using the modified branch and bound method. The domain is initially partitioned into two subdomains and two local minima are identified.

familiarity).

Two different local minima for solution phase α are identified among the two subdomains, where the local minima found in Subdomain 2 yields a null value for π_α (since it was already predicted to be stable) while the other yields a negative value, indicating that it should be added to the system. Since the current example is a binary system at constant temperature and pressure, a maximum of two phases can coexist to prevent contradiction of Gibbs' phase rule. Thus, the general solver proceeds to minimize the Gibbs energy of the system under the assumption that a two-phase miscibility gap represented by solution phase α is stable and A_3B_2 is no longer considered stable.

The sufficient condition for equilibrium is again tested when the necessary conditions for equilibrium have been satisfied. The modified B&B method locates two local minima in π_α that yield null values. To ensure that an additional local minima does not reside in between the aforementioned locations, a refinement technique is performed by constructing a third subdomain (as shown in Figure 3) whereby $\mathcal{L}_i$ and $\mathcal{U}_i$ are defined by the local minima. Minimization of π_α is initialized in the middle of the refined subdomain, as shown in Figure 3. The predicted phase assemblage is thus confirmed to be at thermodynamic equilibrium since the two global minima in π_α are zero.

Figure 3: The subdomains in Figure 2 are further refined by setting the bounds of a third subdomain by the local minima previously identified to ensure that an additional local minima does not reside between these points.

4. Case Studies

Five case studies are evaluated using the grid construction, PSO and B&B methods to evaluate reliability, capability and performance of each method. Reliability is judged based on the ability of each method in finding a known solution. Capabilities are judged based on whether each method is able to handle different types of problems. Finally, performance is judged based on the total number of function evaluations required to perform the global optimization routine. Of course, it is not practical or even meaningful to compare differences in overall computation time since a multitude of other factors would play very important roles (e.g., algorithms used in minimization of G , system size, implementation of algorithms into programming, parallelism, hardware, etc.). Thus, the total number of function evaluations of π_λ will be used as a performance metric to isolate the global optimization performance. Also, this is typically the most expensive operation in the overall global optimization process.

The five cases that are considered are as follows: (I) the relatively simple fictive binary A-B system shown in Figure 1, (II) a relatively simple fictive binary C-D system that is shown in Figure 4, (III) a quinary solution phase that is represented by a regular substitutional model, (IV) an ionic solid solution phase represented by a multi-sublattice model containing a total of 20 compound end members, and (V) a fictive system containing a multi-sublattice phase with 400 compound end members. One of the stopping criteria for all methods is when π_λ is negative, which suggests that solution phase λ should be added to the system. The grid method is otherwise completed when the entire grid has been constructed with a pre-specified resolution. The PSO method is halted after a pre-specified number of iterations have been taken

or when all particles in the swarm converge to a single point. Finally, the B&B method is halted when all sub-domains have been minimized.

Cases I, II and III involve solution phases represented by the regular substitutional solution model, which is generally given by

$$g_\lambda = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} g_{i(\lambda)}^o + RT \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \ln(x_{i(\lambda)}) + g_\lambda^{ex} \quad (13)$$

where $g_{i(\lambda)}^o$ is the reference molar Gibbs energy of pure i , which is computed from a thermodynamic database. The ideal gas constant is R and the absolute temperature is T . The molar excess Gibbs energy of mixing term, g_λ^{ex} , is added to the foregoing equation. This term is a function of the mole fractions of species in the phase and the structure of the equation is model specific. The molar Gibbs energy of a solution phase, g_λ , may also be represented by a multi-sublattice model, which is considered in Cases IV and V, whereby various constituents mix on N_s sublattices, which may or may not be ionic. Such a representation may be expressed via the following general formalism

$$g_\lambda = \sum_{i=1}^{N_\lambda} g_{i(\lambda)}^o \prod_{s=1}^{N_s} y_{i(s)} + RT \sum_{s=1}^{N_s} a_s \sum y_{i(s)} \ln(y_{i(s)}) + g_\lambda^{ex} \quad (14)$$

where $y_{i(s)}$ represents the site fraction of a particular constituent on sublattice s corresponding to species i and a_s is the stoichiometric coefficient of sublattice s . The selection of independent variables is also constrained by charge neutrality given by equation (8). Details regarding each case study are described in the following sub-sections followed by a performance comparison in §4.6.

4.1. Case I

The fictive binary A-B system described earlier is considered in the first case study. The system is comprised of solution phase α and pure stoichiometric phase A_3B_2 at a particular temperature, pressure and elemental composition. The system is initially assumed to be at equilibrium with α and A_3B_2 phases predicted to be stable, as illustrated in Figure 1. However, solution phase α contains a miscibility gap, which corresponds to a lower value of G for $\alpha - \alpha$ than $\alpha - A_3B_2$. For this scenario, $g_{A(\alpha)}^o = 0 \text{ J}\cdot\text{mol}^{-1}$, $g_{B(\alpha)}^o = 300 \text{ J}\cdot\text{mol}^{-1}$, $\Gamma_A = -259.3 \text{ J}\cdot\text{g-at}^{-1}$, $\Gamma_B = -511.0 \text{ J}\cdot\text{g-at}^{-1}$, $T = 1000K$ and $P = 1 \text{ atm}$. The molar Gibbs energy of solution phase α is represented by equation (13) and g_α^{ex} is given by

$$g_\alpha^{ex} = x_A x_B (21000) + x_A x_B^2 (7000) \quad (15)$$

4.2. Case II

Another fictive binary system representing system components C and D is considered in Case II with three solution phases: β , γ and δ . At a particular temperature, pressure and overall composition of $\chi_D = 0.6$, the β phase is believed to be in equilibrium with the γ phase as indicated by the molar Gibbs energy plot in Figure 4. One must therefore confirm that the system is either at true equilibrium or if the predicted assemblage of stable phases must be altered. For this particular scenario, the system is currently not at equilibrium and a combination of the γ phase and the δ phase yield a more negative integral Gibbs energy.

For this case, $g_{C(\beta)}^o = 0 \text{ J}\cdot\text{mol}^{-1}$, $g_{D(\beta)}^o = 12,471 \text{ J}\cdot\text{mol}^{-1}$, $g_{C(\gamma)}^o = 16,628 \text{ J}\cdot\text{mol}^{-1}$, $g_{D(\gamma)}^o = 4,157 \text{ J}\cdot\text{mol}^{-1}$, $g_{C(\delta)}^o = 26,604 \text{ J}\cdot\text{mol}^{-1}$, $g_{D(\delta)}^o = 33,256 \text{ J}\cdot\text{mol}^{-1}$, $\Gamma_C = -3,790 \text{ J}\cdot\text{g}\cdot\text{at}^{-1}$, $\Gamma_D = 2,832 \text{ J}\cdot\text{g}\cdot\text{at}^{-1}$, $T = 1000\text{K}$ and $P = 1 \text{ atm}$. The molar Gibbs energy of solution phase β is represented by equation (13) and g_β^{ex} is given by

$$g_\beta^{ex} = x_C x_D (41,570) + x_C x_D^2 (-58,198) \quad (16)$$

and g_γ^{ex} is

$$g_\gamma^{ex} = x_C x_D (-5,238) \quad (17)$$

and finally, g_δ^{ex} is

$$g_\delta^{ex} = x_C x_D (-59,445) + x_C x_D^2 (-74,826) \quad (18)$$

4.3. Case III

The Mo-Tc-Ru-Rh-Pd system from Kaye *et al* [31] is considered in the third case study. This particular thermodynamic representation of the quinary noble metal system includes the following phases: ideal gas, a non-ideal liquid phase, several stoichiometric solids and four solid solution phases with face centered cubic, body centered cubic, hexagonal closed packed and tetragonal crystal structures. All non-ideal solution phases in this system are represented by a regular substitutional model given by equation (13). Full details of the thermodynamic models involved in this system including all pertinent equations are given by Kaye *et al* [31].

The overall system is comprised of 1 mole of each respective chemical element, and is maintained at a temperature of 1000 K and a hydrostatic pressure of 1 atm. At some point in the iteration cycle, the hexagonal closed packed (HCP) solid solution phase is believed to be in equilibrium with the $\text{Mo}_9\text{Pd}_{11}$ solid phase. To ensure that the integral Gibbs energy of the system is at a global minimum, one must check

Figure 4: The molar Gibbs energy surface for an arbitrary system C-D is shown, which contains three solution phases. The δ phase is at this point believed to be metastable and one must confirm that a combination of β and γ is most stable or if a different combination is more stable. Eight evenly distributed grid points are also constructed in the δ phase.

whether π_λ of any solution phases in the system is negative. For current purposes, only the HCP phase is examined, which is comprised of the following species: Mo, Tc, Ru, Rh and Pd. Upon closer examination, a miscibility gap is found in the HCP phase, whereby a combination of HCP-HCP-Mo₉Pd₁₁ yields a more negative value of G than HCP-Mo₉Pd₁₁.

4.4. Case IV

The fourth case study considers the Pu-U-O ternary system from Guéneau *et al* [32], which includes an ideal gas, non-ideal liquid phase, several pure metallic phases and a (U_y,Pu_{1-y})O_{2±x} fluorite oxide phase. This Mixed Oxide (MOX) is used as a fuel material in some nuclear power reactors. This particular phase is represented by a three sublattice model, whereby the actinoid cations mix on the first sublattice, the oxygen anions and vacancies reside on the second sublattice, and interstitial oxygen anions and vacancies reside on the third sublattice. A full description of this model with comparisons to experimental data is given by Guéneau *et al* [32]. Unlike the previous three cases, Case IV involves an ionic phase; thus, charge neutrality must be taken into account. Also, since this phase is represented by a multi-sublattice phase, one must use the mole fractions of the compound end members as the independent variables.

The overall system is comprised of 0.93 moles of U, 0.07 moles of Pu and 2 moles of O at a temperature of 1000 K and hydrostatic pressure of 1 atm. The solver is believed to have converged with (U_y,Pu_{1-y})O_{2±x} being the only stable phase at equilibrium. Thus, one must ensure that (U_y,Pu_{1-y})O_{2±x} is the only stable

phase at equilibrium and that it does not contain a miscibility gap. After careful examination of π_{MOX} , $(\text{U}_y, \text{Pu}_{1-y})\text{O}_{2\pm x}$ has been confirmed to be the only stable phase under the specified conditions and the system is indeed at equilibrium.

4.5. Case V

The previous four cases either examined relatively simple fictive binary systems that can be graphically plotted – and therefore easily verified – or well established systems that have been published in the open literature. The final case that is considered in this benchmark exercise is a fictive system that contains a very large number of species and has been designed to test any type of numerical global optimization methodology. This phase is based on a three-sublattice model containing ionic and vacant constituents in the same structure as the phase considered in Case IV; however, the first sublattice contains 100 cations with 2 constituents on each of the two remaining sublattices, resulting in a total of 400 compound end members. A practical application of such a large model is the representation of irradiated nuclear fuel, whereby the process of nuclear fission yields every chemical element on the period table with an atomic number below 96 [33]. Although some of the fission products may be of very low concentration, they may nonetheless have significant radiological consequences and may be necessary to consider.

Due to the very large number of parameters involved with this phase, it is not practical to provide all details but instead to give an indication of how the fictive phase was fabricated. The fictive phase was designed to be representative of 60 chemical elements with 1-3 constituents per chemical element, whereby the cations had a positive charge ranging from +3 to +5 while the constituents on the anionic and interstitial sublattices had a charge of -2 (i.e., oxygen) or null (i.e., vacancy). The reference molar Gibbs energy of each compound end member was assigned a random value between -200,000 J·g-at⁻¹ and -450,000 J·g-at⁻¹. Excess mixing parameters were created such that one cation would mix with the following cation in the list of constituents on the first sublattice with a mixing parameter that was randomly assigned between 100,000 and -100,000 for zeroth order terms and between 1000 and -1000 for first order terms.

4.6. Benchmark Comparison

Table 2 compares the total number of function evaluations for the five case studies using the grid construction, PSO and B&B algorithms. Since the performance and success of all of the foregoing algorithms are strongly influenced by several decisions made in their implementation into a thermodynamic solver, two different likely implementations of the grid construction and PSO algorithms are compared. For instance, coarse and fine grid resolutions are implemented in the grid construction method, whereby the former used 8 evenly spaced grid points between each species whereas the latter used 100 in a similar fashion as what

was described in §3.2.1. Also, two different implementations of the PSO algorithm are explored, which will be referred to henceforth as PSO(A) and PSO(B). The former constrains the maximum incremental change in $\mathbf{x}_p$ to 0.1, whereas the latter permits the maximum magnitude of the velocity vector to increase with the iteration cycle as in equation (11). For PSO(B), $v_{min} = 0.05$ and $v_{max} = 1$.

In addition to important decisions made in the grid spacing or maximum incremental change of the independent variables, there are other variations that can affect the number of function evaluations that are not controllable and are up to chance. Obviously, the number of function evaluations with a stochastic method is not definite since it is by definition dependent on randomness. Additionally, the number of function evaluations in the grid construction method may vary depending on the order of grid points constructed, which may terminate the operation at different stages if a negative value of π_λ is found. This is why some cells in Table 2 have a range of values.

The grid construction method was able to find the minimum in the first four case studies with a fine resolution grid; however, the coarse grid failed in a number of cases, which indicates that grid resolution is crucial to its success. Although this method was successful with a high resolution grid, the number of function evaluations required for the larger systems was exceptionally high. Also, note that the number of function evaluations for Case IV is less than what is computed with equation (12) because most combinations are rejected when charge neutrality is not satisfied. Thus, one must induce an additional overhead calculation to ensure charge constraints are met.

The PSO method was overall fairly successful, but it was not always able to reach the global minimum with a maximum increment of $\delta = 0.1$ in PSO(A). Taking the first case study as an example, an initial particle would be released near pure A and then attempt to move towards pure B with an increment of 0.1. This particle would overshoot the local valley near 0.05, say from an initial value near α_1 to α_2 in Figure 1. Then, the same particle would continue on the same trajectory with a velocity vector computed with equation (9) that is dominated by the inertial term and the term that attracts that particle to the best estimate of the swarm (i.e., $\chi_B \approx 0.9$). As this particle approaches the best estimate of the swarm, the attraction component of equation (9) to the global best estimate weakens while the component that attracts p to the local best estimate (i.e., near α_2) strengthens, resulting in the particle reversing direction. This particle may repeatedly reverse direction in the vicinity of $0.3 \leq \chi_B \leq 0.6$ for Case I and is unable to escape to either the best estimate of the local particle or that of the swarm. Note that PSO(A) had greater success for Case II because the molar Gibbs energy curve of the metastable δ phase has a concave curvature.

The maximum increment of $\mathbf{x}_p$ in PSO(A) is 0.1 while PSO(B) varies with m . For the first case study, the global minimum is in fact missed with PSO(A) whereby one of the particles surpasses a minima because the increment was too large. Unlike many deterministic methods, the local gradient of the functional value is not taken into consideration, which would otherwise follow the gradient to the local minima. Also, in addition to being more likely to miss locating a minima, the performance can in fact be worse with a coarser maximum increment size with PSO(A) because a particle may continuously move back and forth without making progress. The PSO method was unable to handle Cases IV and V due to the inability to enforce charge neutrality constraints in the current implementation. Overall, the PSO(B) method provides good reliability and performance, but the specific implementation of PSO discussed herein is not well suited to handle ionic phases.

In the B&B method, the maximum incremental change in the position vector $\mathbf{x}$ is also constrained by 0.1. Unlike the PSO(A) approach, the efficacy of the search is not as sensitive to large changes in $\mathbf{x}$ because the search exploits the local topology of the numerical landscape. The main decisions that are made in executing the B&B method are the locations of where particles are released, the maximum incremental change and the line search method. Multiple scenarios were considered for each case that changed the order in which particles are released. A simple approximate line search is performed to ensure that the Wolfe conditions have been satisfied. In all five scenarios, the B&B method was able to find the global minimum. Furthermore, it was able to do so with the fewest number of function evaluations amongst all numerical methods evaluated herein.

Table 2: The total number of function evaluations of π_λ are summarized for five benchmark problems using the grid, Particle Swarm Optimization (PSO) and Branch & Bound (B&B) methods. Cells marked with * indicate failure to find the global minimum and X corresponds to problems that cannot be solved with a particular method.

Method	Case I	Case II	Case III	Case IV	Case V
Coarse Grid ($\epsilon = 8$)	8*	8*	20	X	X
Fine Grid ($\epsilon = 100$)	4 – 101	38 – 53	19 – 10^6	1.1×10^{20}	X
PSO (A)	86 – 200*	7 – 12	120 – 500*	X	X
PSO (B)	8 – 12	9 – 16	25 – 45	X	X
B&B	2 – 4	4 – 6	3 – 23	40	1.9×10^3

5. Discussion

All global optimization algorithms from both deterministic and stochastic approaches have their advantages and disadvantages. No global optimization method is universally superior to all others for all types of problems and the success of any approach is generally problem specific. For the case of Gibbs energy minimization, the driving force π_λ is smooth, continuous and the independent variables (i.e., $x_{i(\lambda)}$) have upper and lower bounds. Also, in comparison to other global optimization problems, the objective function does not contain many local minima; however, the number of independent variables can be relatively large.

In the broad context of global optimization algorithms, deterministic methods are generally effective at reaching a global optimum since the search exploits the local gradient of the functional surface; however, a common issue with deterministic methods is that the computational expense can be quite high since a system of linear equations representing the Hessian matrix must be solved in order to compute a new set of decision variables. Also, sufficiently sweeping the search space tends to greatly increase computational expense. Stochastic methods, on the other hand, do not require the solution of a system of linear equations, while the search space is traversed by some random trajectory of a single point or assemblage of points. These methods tend to cover a large portion of the search space effectively, but can have difficulty at times in finding a minimum.

The PSO method can be quite powerful and can be effectively applied to Gibbs energy minimization problems. Although the first implementation of PSO (i.e., PSO(A)) in the benchmark analysis in §4 was ineffective, implementation of PSO with more appropriate constraints of the velocity vector (i.e., PSO(B)) proved to be more robust and efficient. Notwithstanding the success demonstrated with PSO(B) in finding a global minimum in Cases I, II and III, and success reported in the literature [17], one issue in its implementation is in satisfying charge neutrality constraints in ionic phases. Without having a method to sufficiently and efficiently address this particular concern, the PSO method is not generally applicable to Gibbs energy minimization problems involving ionic phases.

The grid construction method has been used in a number of commercial thermodynamic solvers. Although it is quite simple to implement and reliable for fairly simple problems, its success depends on user intervention (e.g., deciding whether to use a normal or dense grid). Furthermore, its behaviour and success with higher order systems is unclear since the method has not been described in detail in the open literature. As has been demonstrated in Tables 1 and 2, the number of function evaluations required to sufficiently discretize the domain space increases at a high rate with respect to the number of solution species. Of course, this depends on the specific implementation of the method.

For minimizing π_λ in thermodynamic equilibrium problems, the B&B method has proven to be reliable, flexible and computationally efficient. The method was superior in solving all five case studies with greater success and fewer function evaluations than the grid construction and PSO methods. It was the only method able to solve Case V using the implementations described in this article. Moreover, the generality of the B&B method has been demonstrated by handling a variety of model types, including ionic solid solutions. For the problem at hand, solving the system of linear equations represented by the Hessian matrix is not a major concern – as is often the case with deterministic methods – since exploiting a symmetric arrow matrix structure of the Hessian significantly reduces the computational expense. A derivation of equations is given in Appendix B.

6. Conclusion

Several stochastic and deterministic global optimization algorithms are reviewed with application to computing thermodynamic equilibria. The grid construction, Particle Swarm Optimization (PSO) and Branch & Bound (B&B) methods are compared with five case studies of varying complexity. Although the grid construction method is quite simple and straightforward, it is not always reliable with a coarse grid and the number of function evaluations required to reliably handle large phases can be quite high in large systems. While the PSO method is found to be reliable with a modest number of function evaluations, it does not lend itself very well to a broad set of problems, particularly ionic phases that require charge neutrality constraints to be respected. A modified B&B method has been shown to be reliable, require very few function evaluations and is able to easily handle a wide variety of phase types. These qualities are particularly desirable for thermodynamic calculations of large complex systems and when integrated into multi-physics codes where flexibility, reliability and performance are of paramount importance.

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Appendix A. Derivation of the Lagrangian Function of the Driving Force

The Lagrangian function of the driving force of solution phase λ is defined as:

$$L_\lambda = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j \right) - \pi_\lambda \left(\sum_{i=1}^{N_\lambda} x_{i(\lambda)} - 1 \right) \quad (\text{A.1})$$

where π_λ represents the driving force for solution phase λ . Within this procedure, all global variables are held constant (i.e., Γ_j) where all local variables are adjusted. The local variables are $x_{i(\lambda)}$ and π_λ , resulting in a system with $N_\lambda + 1$ variables for a particular solution phase λ . Note that $\mu_{i(\lambda)}$ is a function of $x_{i(\lambda)}$. The Lagrangian function has a minimum value when $\nabla L = 0$. Differentiating L_λ with respect to $x_{i(\lambda)}$ and using the Gibbs-Duhem equation yields,

$$\frac{\partial L_\lambda}{\partial x_{i(\lambda)}} = \mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j + 1 - \pi_\lambda \quad (\text{A.2})$$

and differentiating L_λ with respect to π_λ yields,

$$\frac{\partial L_\lambda}{\partial \pi_\lambda} = 1 - \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \quad (\text{A.3})$$

The system of non-linear equations above can be solved from a second order Taylor series expansion of the Lagrangian function,

$$\nabla^2 L_\lambda \delta y = -\nabla L_\lambda \quad (\text{A.4})$$

where $\delta y = (\delta x, \delta \pi)^T$ is a column vector of unknown variables. The second order partial derivatives corresponding to the mole fractions are:

$$\frac{\partial^2 L_\lambda}{\partial x_{i(\lambda)}^2} = \frac{1}{x_{i(\lambda)}} \quad (\text{A.5})$$

and,

$$\frac{\partial^2 L_\lambda}{\partial x_{i(\lambda)} \partial x_{j(\lambda)}} = 0 \quad (\text{A.6})$$

Also, the second order partial derivatives of the Lagrangian function involving π_λ are:

$$\frac{\partial^2 L_\lambda}{\partial \pi_\lambda \partial x_{i(\lambda)}} = -1 \quad (\text{A.7})$$

and,

$$\frac{\partial^2 L_\lambda}{\partial \pi_\lambda^2} = 0 \quad (\text{A.8})$$

The foregoing equations can be extended to handle ionic phases, which must necessarily satisfy charge neutrality constraints through the following formulation

$$L_\lambda = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j \right) - \pi_\lambda \left(\sum_{i=1}^{N_\lambda} x_{i(\lambda)} - 1 \right) - \pi_e \left(\sum_{i=1}^{N_\lambda} a_{i,e} x_{i(\lambda)} - 1 \right) \quad (\text{A.9})$$

where π_e is the Lagrangian multiplier of the electronic component. Solving the first order partial differential gives

$$\frac{\partial L_\lambda}{\partial \pi_e} = 1 - \sum_{i=1}^{N_\lambda} a_{i,e} x_{i(\lambda)} \quad (\text{A.10})$$

and the second order term

$$\frac{\partial^2 L_\lambda}{\partial \pi_e^2} = 0 \quad (\text{A.11})$$

and finally,

$$\frac{\partial^2 L_\lambda}{\partial \pi_e \partial x_i} = -a_{i,e} \quad (\text{A.12})$$

The above system of equations can be solved fairly easily to determine a combination of $x_{i(\lambda)}$ that yields a minimum in the driving force π_λ . A procedure that efficiently solves this unique system of linear equations is described in Appendix B. One should also employ an appropriate line search algorithm to ensure that the Wolfe conditions have been satisfied and to prevent the local system from escaping the feasible region (i.e., $0 < x_{i(\lambda)} < 1$). Also, it is important that the step length constrains the maximum change in the mole fraction, otherwise a local minima may be overlooked.

An effective approach computes an initial minimum steplength that satisfies the following two conditions: first, the maximum change in $x_{i(\lambda)}$ is less than or equal to 0.2; second, if any $x_{i(\lambda)}$ tends to be negative, a steplength is computed that reduces $x_{i(\lambda)}$ by two orders of magnitude. After an initial step length is computed and the Lagrangian is re-evaluated. If the Wolfe conditions are not satisfied, the steplength is halved and the Lagrangian re-evaluated once again until the Wolfe conditions have been satisfied.

Appendix B. An Efficient Method for Solving a System of Linear Equations with a Symmetric Arrow Matrix

Observe that the Hessian matrix derived in the previous section is a symmetric arrow matrix. Specifically, the matrix contains a single diagonal band and the far right column and bottom row are filled (except for the extreme right corner). Not only is the matrix symmetric, but the far right column and bottom row contain a constant value. Computational expense can be significantly reduced if one exploits the unique

characteristics of this particular system of linear equations.

A general linear equation solver (such as one based on Gaussian elimination, LU decomposition or an iterative method) is not required to solve this particular problem. One can solve this system of linear equations by performing Gaussian elimination on *only* the bottom row followed by back substitution to solve the solution vector. Also, one can reduce memory requirements by recognizing that the Hessian matrix does not have to be constructed, which can be replaced by the diagonal vector and a scalar (representing the far right column).

References

References

- [1] C. McDonald and C. Floudas, “Global optimization and analysis for the Gibbs free energy function using the UNIFAC, Wilson, and ASOG equations,” *Industrial and Engineering Chemistry Research*, vol. 34, pp. 1674–1687, 1995.
- [2] A. Bonilla-Petriciolet, S. Fateen, and G. Rangaiah, “Assessment of capabilities and limitations of stochastic global optimization methods for modeling mean activity coefficients of ionic liquids,” *Fluid Phase Equilibria*, vol. 340, pp. 15–26, 2013.
- [3] A. Bonilla-Petriciolet and J. G. Segovia-Hernández, “Particle swarm optimization for phase stability and equilibrium calculations in reactive systems,” 19th European Symposium on Computer Aided Process Engineering (ESCAPE19), 2009.
- [4] V. Bhargava, S. Fateen, and A. Bonilla-Petriciolet, “Cuckoo search: A new nature-inspired optimization method for phase equilibrium calculations,” *Fluid Phase Equilibria*, vol. 337, pp. 191–200, 2013.
- [5] K. Shobu, “CaTCalc: New thermodynamic equilibrium calculation software,” *CALPHAD*, vol. 33, pp. 279–287, 2009.
- [6] Y. Teh and G. Rangaiah, “Tabu search for global optimization of continuous functions with application to phase equilibrium calculations,” *Computers and Chemical Engineering*, vol. 27, pp. 1665–1679, 2003.
- [7] C. Harvie, J. Greenberg, and J. Weare, “A chemical equilibrium algorithm for highly non-ideal multi-phase systems: Free energy minimization,” *Geochimica et Cosmochimica Acta*, vol. 51, pp. 1045–1057, 1987.
- [8] M. Piro, S. Simunovic, T. Besmann, B. Lewis, and W. Thompson, “The thermochemistry library THERMOCHEMICA,” *Computational Materials Science*, vol. 67, pp. 266–272, 2013.

- [9] C. Newman, G. Hansen, and D. Gaston, “Three dimensional coupled simulation of thermomechanics, heat and oxygen diffusion in UO_2 nuclear fuel rods,” *Journal of Nuclear Materials*, vol. 392, pp. 6–15, 2009.
- [10] R. Horst, P. Pardalos, and N. Thoai, *Introduction to Global Optimization (Nonconvex Optimization and its Applications)*. Springer, 2nd ed., 2000.
- [11] W. White, S. Johnson, and G. Dantzig, “Chemical equilibrium in complex mixtures,” *Journal of Chemical Physics*, vol. 28, no. 5, pp. 751–755, 1958.
- [12] G. Eriksson and E. Rosen, “General equations for the calculation of equilibria in multiphase systems,” *Chemica Scripta*, vol. 4, pp. 193–194, 1973.
- [13] B. Sundman, B. Jansson, and J.-O. Andersson, “The Thermo-Calc databank system,” *CALPHAD*, vol. 9, no. 2, pp. 153–190, 1985.
- [14] M. Piro, T. Besmann, S. Simunovic, B. Lewis, and W. Thompson, “Numerical verification of equilibrium thermodynamic computations in nuclear fuel performance codes,” *Journal of Nuclear Materials*, vol. 414, no. 3, pp. 399 – 407, 2011.
- [15] M. Hillert, “Some viewpoints on the use of a computer for calculating phase diagrams,” *Physica*, vol. 103B, pp. 31–40, 1981.
- [16] H. Lukas, S. Fries, and B. Sundman, *Computational Thermodynamics: The Calphad Method*. Cambridge University Press, 2007.
- [17] H. Zhang, A. Bonilla-Petriciolet, and G. Rangaiah, “A review on global optimization methods for phase equilibrium modeling and calculations,” *The Open Thermodynamics Journal*, vol. 5, pp. 71–92, 2011.
- [18] B. Sundman, X.-G. Lu, and H. Ohtani, “The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software,” *Computational Materials Science*, vol. 101, pp. 127–137, 2015.
- [19] C. Floudas, *Deterministic Global Optimization: Theory, Methods and Applications*. Springer, 1999.
- [20] M. Piro, J. Banfield, K. Clarno, S. Simunovic, T. Besmann, B. Lewis, and W. Thompson, “Coupled thermochemical, isotopic evolution and heat transfer simulations in highly irradiated UO_2 nuclear fuel,” *Journal of Nuclear Materials*, vol. 441, pp. 240–251, 2013.
- [21] A. Bonilla-Petriciolet, J. G. Segovia-Hernández, F. Castillo-Borja, and U. I. Bravo-Sánchez, “Thermodynamic calculations for chemical engineering using a simulated annealing optimization method,” 17th European Symposium on Computer Aided Process Engineering (ESCAPE17), 2007.

- [22] G. P. Rangaiah, "Evaluation of genetic algorithms and simulated annealing for phase equilibrium and stability problems," *Fluid Phase Equilibria*, vol. 187, pp. 83–109, 2001.
- [23] J. A. Fernández-Vargas, A. Bonilla-Petriciolet, and J. G. Segovia-Hernández, "An improved ant colony optimization method and its application for the thermodynamic modelling of phase equilibrium," *Fluid Phase Equilibria*, vol. 353, pp. 121–131, 2013.
- [24] M. Srinivas and G. Rangaiah, "Implementation and evaluation of random tunneling algorithm for chemical engineering applications," *Computers and Chemical Engineering*, vol. 30, pp. 1400–1415, 2006.
- [25] J. Kennedy and R. Eberhart, "Particle swarm optimization," *Proceedings of IEEE International Conference on Neural Networks*, 1995.
- [26] J. Barhen, V. Protopopescu, and D. Reister, "TRUST: a deterministic algorithm for global optimization," *Science*, vol. 276, pp. 1094–1097, 1997.
- [27] J. Falk and R. Soland, "An algorithm for separable nonconvex programming problems," *Management Science*, vol. 15, no. 9, pp. 550–569, 1969.
- [28] S.-L. Chen, K.-C. Chou, and Y. Chang, "On a new strategy for phase diagram calculation: 1. basic principles," *CALPHAD*, vol. 17, no. 3, pp. 237–250, 1993.
- [29] S.-L. Chen, K.-C. Chou, and Y. Chang, "On a new strategy for phase diagram calculation: 2. binary systems," *CALPHAD*, vol. 17, no. 3, pp. 287–302, 1993.
- [30] L. Jaulin, M. Kieffer, O. Didrit, and E. Walter, *Applied Interval Analysis*. Berlin: Springer, 2001.
- [31] M. Kaye, B. Lewis, and W. Thompson, "Thermodynamic treatment of noble metal fission products in nuclear fuel," *Journal of Nuclear Materials*, vol. 366, pp. 8–27, 2007.
- [32] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F. D. Bruycker, D. Manara, and R. J. Konings, "Thermodynamic modelling of advanced oxide and carbide nuclear fuels: Description of the U-Pu-O-C systems," *Journal of Nuclear Materials*, vol. 419, no. 1-3, pp. 145–167, 2011.
- [33] B. Lewis, W. Thompson, and F. Iglesias, *Comprehensive Nuclear Materials: Fission Product Chemistry in Oxide Fuels*. Elsevier, 2012.