58. Solving Phase Equilibrium Problems by Means of Avoidance-Based Multiobjectivization

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Phase-equilibrium problems are good examples for real-world engineering optimization problems with a certain characteristic. Despite their low dimensionality, finding the desired optima is difficult as their basins of attraction are small and surrounded by the much larger basin of the global optimum, which unfortunately resembles a physically impossible and therefore unwanted solution. We tackle such problems by means of a multiobjectivization-assisted multimodal optimization algorithm which explicitly uses problem knowledge concerning where the sought solutions are not in order to find the desired ones. The method is successfully applied to three phase-equilibrium problems and shall be suitable also for tackling difficult multimodal optimization problems from other domains.

58.1 Coping with Real-World Optimization Problems

A multitude of methods from within and beyond *evolutionary computation* (EC) has been applied to real-valued multimodal optimization problems. These are generally considered the harder, the more basins of attraction they contain, and the less smooth the fitness landscape is. Additionally, a search space that extends over a large number of dimensions is said to complicate search for the desired global or good local optima [58.1].

However, in a real-world setting, even a low-dimensional problem may turn out to be quite difficult. This can stem from different factors, one of which would be a very small extent of the basins that contain the sought optima. Figure 58.1 visualizes the fitness landscape of an optimization problem that possesses this property. The application background will be detailed in Sect. 58.2, but for now it suffices to know that there are only two variables a and b, and that the desired minima (function values do not depend on variable order and are thus symmetric to the main diagonal) are located near (0.650,0.001) and (0.001,0.650), respectively. It is easy to see that the appropriate basins are small; in the figure, they are hardly recognizable at all.

Another complicating factor would be uncertainty about the relative target function value of the sought optima. If it is not a priori known whether we are looking for a global or only a certain local optimum, there is no way around enumerating all existing optima and choosing the *right* solution out of these afterward. Such difficulties may occur in cases where it is not possible to integrate the whole available application specific knowledge into the established target function, i. e., if its value must be obtained by simulation and the exist-

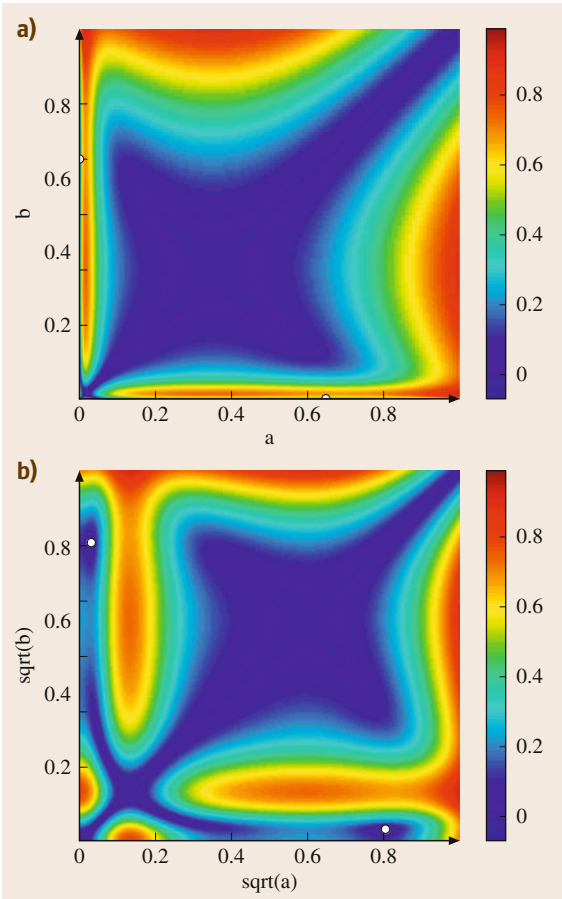

Fig. 58.1a,b Visualizations of the two-dimensional example problem. In the bottom panel, the search space is transformed by a square root. The desired optima are marked with *white dots*. Note that the diagonal consists of globally optimal but undesired (trivial) solutions

ing simulation tool is not able to represent all important features of the real system.

Obviously, there are several workarounds to overcome the difficulties imposed by this problem:

- Applying a transformation to the search space, so that the local optima at the lower boundaries occupy more space. This is shown in Fig. 58.1.
- Only initializing the optimization algorithm with solutions on the boundaries of the search space. In this case, we sometimes start from very near to the local optima, and thus have a higher chance to find them.
- Exploiting the symmetry of the landscape by a special representation. This can be done by enforcing $a \geq b$ and would help, e.g., recombination operators of evolutionary algorithms (EAs).

However, all these approaches are dependent on the location of the desired optima. Any algorithm exploiting this expert knowledge would neccessarily show a worse performance on problems without these special features, as predicted by the *no free lunch* theorem [58.2]. Instead, a more general method, which uses information on where the desired optima is *not*, will be discussed and evaluated in this chapter.

Many different EAs may be used to tackle this global or multimodal optimization problem because they are able to detect several optima simultaneously or subsequently. The latter may be achieved by multistart approaches as sequential niching [58.3], whereas the former is established by means of diversity maintenance. That is, candidate solutions of the search populations are prevented from converging to the same region by implicitly or explicitly keeping them apart [58.4]. Prominent examples are crowding [58.5] and fitness sharing [58.6], and their successors. More recent approaches include, but are not limited to UEGO [58.7], clearing [58.8], species conservation [58.9], clustering-based niching [58.10], and cellular EA (CEA) [58.11]. Although there is no commonly accepted formal definition of what a niching method is [58.12], most of these algorithms may be subsumed under the term *niching EA*. They all use the distance between candidate solutions (diversity) as an implicit criterion which shall be maximized.

However, nothing prevents us from utilizing a diversity criterion directly. A step into this direction has been taken in the shifting balance GA [58.13]. But although it employs a separate diversity evaluation via subpopulation distance computation, it finally resorts to a single objective by weighting the distance and target function values.

In [58.14], we established a more radical approach and employ diversity in search space as an additional objective and treat the resulting combined problem by an *evolutionary multiobjective algorithm* (EMOA). The expected benefit is twofold:

- It enables placing solution candidates in basins that would otherwise go unnoticed due to their small size.
- We obtain a good overview of the available *interesting* search space regions in a single run.

As we presume that this approach is not only applicable to the thermodynamic problems treated in

this work but also to real-valued engineering problems with similar properties, it is also followed and further extended here. Other related multiobjectivization approaches are discussed in Sect. 58.3 after introducing the problem context.

58.2 The Phase-Equilibrium Calculation Problem

The knowledge of phase equilibria is required for the design and optimization of separation processes which are essential parts of typical chemical plants. The aim of a *phase-equilibrium calculation* is to quantitatively relate the variables (in particular, temperature T, pressure p, and mole fraction x) which describe the state of equilibrium of two or more homogenous phases [58.15].

In any problem concerning the equilibrium distributions of k components between two phases, one must always begin with the equality of the chemical potential μ as

$$\forall i \in \{1, \ldots, k\} : \mu_i' = \mu_i'' \,. \tag{58.1}$$

To establish the relation of μ_i' (We use the domain-specific notation with upper index denoting different phases and lower index standing for separate substances.) to T, p, and x_i', it is convenient to introduce a certain auxiliary function such as the fugacity coefficient $\varphi_i'(T, p, x_i')$, which can be calculated by a thermodynamic model. Then, (58.1) can be rewritten as

$$\forall i \in \{1, \ldots, k\} : x_i' \cdot \varphi_i' = x_i'' \cdot \varphi_i'' \,. \tag{58.2}$$

Typically, the calculation is performed at constant temperature and pressure, and the remaining concentrations x_i' and x_i'', respectively, are to be found. The fugacity coefficient φ_i of component i in the mixture is calculated as

$$\ln \varphi_i = \frac{\mu_i^{\mathrm{res}}}{RT} - \ln Z \,, \tag{58.3}$$

with Z being the compressibility factor, defined as

$$Z \equiv \frac{pv}{RT} \,, \tag{58.4}$$

where v is the molar volume, and R is the gas constant. The residual chemical potential μ_i^{res} is given by

$$\mu_i^{\mathrm{res}} = a^{\mathrm{res}} + RT(Z-1) + \frac{\partial a^{\mathrm{res}}}{\partial x_i} - \sum x_\ell \left(\frac{\partial a^{\mathrm{res}}}{\partial x_\ell} \right) \,, \tag{58.5}$$

where $(\partial a^{\mathrm{res}} / \partial x_i)$ is a partial derivative of the residual Helmholtz energy with respect to the mole fraction stated in the denominator, while all other mole fractions are considered constant.

The residual Helmholtz energy according to the perturbed chain statistical associating fluid theory (PC-SAFT) is considered as the sum of different contributions resulting from repulsion (hard chain), van der Waals attraction (dispersion), and hydrogen bonding (association)

$$a^{\mathrm{res}} = a^{\mathrm{hc}} + a^{\mathrm{disp}} + a^{\mathrm{assoc}} \,. \tag{58.6}$$

The detailed equations for each contribution can be found in [58.16] and [58.17].

Solving phase-equilibrium problems according to (58.2) may lead to trivial solutions, i. e., $x_i' = x_i''$, which are mathematically correct but have no physical meaning (except at the so-called critical demixing point). To avoid obtaining them, the initial guesses for the minimization procedure may not be too far away from the correct solutions, provided that the correct solutions are known.

In the case of polymer solutions, initialization is very critical, because the concentration of the polymer in the solvent-rich phase can be in the magnitude of 10^{-20}, which is a numerical challenge for simulation programs [58.18]. Another difficulty arises as the number of components in the mixture increases. All these challenges point out the need for a robust algorithm to solve the phase-equilibrium calculation for an arbitrary number of components and phases, and which is also applicable to polymer solutions.

Figure 58.1 actually shows a phase-equilibrium problem, namely a simple two-component mixture of water and pentanol. This type of liquid–liquid equilibrium (LLE) data are necessary for the design and optimization of liquid–liquid extractors and decanters. The two variables correspond to the concentrations of water in the water-rich phase (for the larger of the two) and in the pentanol-rich phase (for the smaller one). Under the assumption that $a > b$, and that w stands for water and p for pentanol, we have $a = x_{\mathrm{w}}'$, and $b = x_{\mathrm{w}}''$.

The remaining mole fractions x'_p and x''_p can be obtained indirectly as $x'_p = 1 - x'_w$ and $x''_p = 1 - x''_w$, because for every phase, the following equality holds:

$$\sum_{i=1}^{k} x'_i = \sum_{i=1}^{k} x''_i = 1 \,. \tag{58.7}$$

For this two-component problem, two equations of type (58.2) have to be satisfied, resulting in two error values $e_w = |x'_w \varphi'_w - x''_w \varphi''_w|$ and $e_p = |x'_p \varphi'_p - x''_p \varphi''_p|$. A feasible solution to the problem shall exhibit errors below 10^{-10} due to practical requirements. In the following, e_w and e_p are aggregated into a single target function value by using the sum of squares, which is to be minimized (note the vector notation)

$$f_1(\boldsymbol{x}', \boldsymbol{x}'') = e_w^2 + e_p^2 \,. \tag{58.8}$$

Table 58.1 The sought optima at different temperatures

Mole fraction	40 °C	60 °C	90 °C
x'_w	0.74698	0.7097	0.65084
x''_w	0.00020913	0.00038142	0.00082809

In Fig. 58.1, (58.8) is modeled at a temperature of 90 °C, for which the sought optimum is located near the coordinates (0.650,0.001). As system properties change with temperature and pressure, the pursued optimum also moves through the search space. Table 58.1 depicts approximate solutions for different temperatures and constant pressure of 1.0132 bar. The trivial solutions are the only feature representative for all phase-equilibrium problems. Thus, this is the only information that shall be exploited in the following.

58.3 Multiobjectivization-Assisted Multimodal Optimization: MOAMO

As seen in Sect. 58.1, the optimization problem at hand is inherently multimodal. That is, local optimization schemes are only successful if started from a region near the desired nontrivial solution. To make things worse, the basin of attraction of the undesired trivial solutions may largely dominate the search space as found for the very simple LLE problem (two phases, two components: water/pentanol). Hitting the basin of attraction of the desired solution can be very difficult, and if failing on this, the final outcome of quasi-Newton or similar algorithms will be a trivial solution.

Stochastic optimization methods like EAs and other metaheuristics employ a more globally oriented optimization scheme. Several attempts using these methods have been tried on equilibrium detection problems in recent years, namely genetic algorithms (GA) and simulated annealing in [58.19] or differential evolution (DE) and tabu search (TS) in [58.20]. The algorithms have been mostly used in their canonical form with some parameters tuning and a concluding local optimization step by means of a quasi-Newton method. Alternative approaches applied artificial neural networks for learning and predicting phase equilibria as in [58.21], the authors of which evolve the neural networks by means of genetic programming (GP), and [58.22], where the authors employ a real-coded GA to optimize initial weights and biases of the neural network before it is further refined using a quasi-Newton method. Where enough training data is available, the binodal curves of equilibria can be learned and predicted for the missing areas.

Some recent metaheuristic attempts concentrate on the global (multimodal) nature of the optimization problem to find equilibrium points for rather difficult systems where global optima are located in relatively small basins. [58.23] use tabu search, [58.24] a random tunneling method, and [58.25] a DE hybrid with TS components. While we agree that *looking elsewhere* for even better solutions is mandatory for a multimodal problem, it may be even more rewarding to obtain a good overview over large portions of the search space before climbing down into the individual optima. This has been attempted by using a refined version of the algorithm of [58.26] which has been applied to phase stability problems by [58.27]. The base algorithm GLOBAL has been developed further in [58.28]. As the latter methods start from a random sample, it may however happen that either the initial sample is too small so that important optima are missed, or it is relatively large and thus costly.

The optimization concept suggested in this work therefore relies on an evolutionary multiobjective algorithm (EMOA) approach in order to generate a spectrum of possible near-optimal solutions before applying a local search method on these. We term it *multiobjectivization-assisted multimodal optimization* (MOAMO). The method was successfully applied

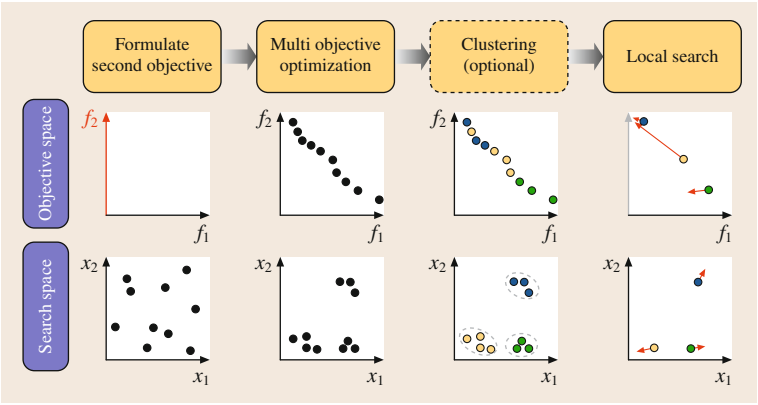

Fig. 58.2 The general concept of MOAMO and its influence on search and objective space

onto the two-phase 2-component water/pentanol system in [58.14]. Here, we demonstrate that it is viable for more complicated equilibrium problems with more phases and components. Although not yet tried on polymer problems, this ultimate goal seems to be in reach as very small basins of attraction can be attained reliably.

Figure 58.2 shows the main concept of the MOAMO approach. The key idea is to use a population-based multiobjective algorithm as a preprocessing step for generating search points in the different basins of attraction of the tackled problem, the basin of the nontrivial optimum being among them. To do this, the practitioner first has to formulate an additional objective function. This second objective is then employed to obtain good coverage of the search space despite the high attraction of certain areas. We label this type of multiobjectivization *avoidance-based* because application knowledge about where the sought optimum is *not* helps to transform the single-objective optimization problem into a multiobjective one that is easier to solve. More precisely, it enables detecting several different basins, among them many that would most likely have gone unnoticed with the single-objective approach alone.

For this specific application, the distance to the trivial solution (equal concentrations) is taken into account. From then on, the system can work autonomously. In the next step, the multiobjective optimization is carried out. The obtained search points then are fed one by one into a local optimization method, until a satisfying nontrivial solution is found. For this local search, only the original objective is relevant. We employed the algorithm of [58.29] and the covariance matrix adaptation evolution strategy (CMA-ES) of [58.30] for this last step. The experimental results suggest that especially the latter seems well suited for the task. However, one may resort to another method here (e.g., quasi-Newton or similar standard optimization algorithms as described in [58.31]) if it is deemed more appropriate. To avoid superfluous local optimization steps on candidate solutions that are close to each other, this phase may be prepended with a clustering step so that one tries a representative of each *group* of solutions first and then proceeds in a round robin fashion.

The idea of simplifying a difficult single-objective problem by a multiobjective approach has some precursors in evolutionary computation and has been coined as multiobjectivization by [58.32]. The approach can be divided into two general categories, namely multiobjectivization by adding objectives and multiobjectivization by the decomposition of a scalar objective function.

For the latter one, it can be proven that the approach can only decrease the number of local optima [58.33]. It was for example successfully applied to protein structure prediction problems in [58.34, 35]. MOAMO belongs to the category of multiobjectivization by adding objectives. No theoretic guarantees of benefits can be given [58.36] for this approach, but nonetheless it has already been tried in several different ways [58.37–40]. However, these applications somewhat remain in the tradition of evolutionary multiobjective algorithms that already contain diversity preserving mechanisms. The second objectives suggested all refer to the current population or single individuals thereof and do not take characteristics of the actual problem into account. MOAMO strongly differs as instead of a *population-relative*, it employs an *absolute*

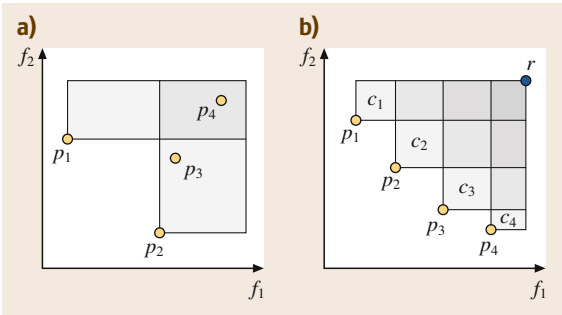

Fig. 58.3 **(a)** Pareto dominance for minimization: $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$ are non-dominated, $\boldsymbol{p}_3$ is dominated by $\boldsymbol{p}_2$, and $\boldsymbol{p}_4$ is dominated by $\boldsymbol{p}_1$ and $\boldsymbol{p}_2$. **(b)** A non-dominated front between objectives f_1 and f_2, consisting of points $\boldsymbol{p}_1$ to $\boldsymbol{p}_4$. c_1 to c_4 denote the hypervolume contribution of each point (the space not covered by any other point) against the reference point $\boldsymbol{r}$

distance objective, namely the distance to the known trivial solutions. The MOAMO approach is therefore especially well suited to phase equilibrium problems, as the fugacity equations do not allow to directly conclude where the sought solution is, but at least they provide information on where it is not. It has been demonstrated in [58.14] that by using the multiobjective EA as preprocessing step, the important basin can be located with a much smaller amount of function evaluations than would be needed by sampling the search space randomly, even if the basin is very small.

In the following, basic EMOA concepts are summarized and the particular multiobjective optimization algorithm employed in our experiments is introduced, namely the SMS-EMOA by [58.41] and [58.42].

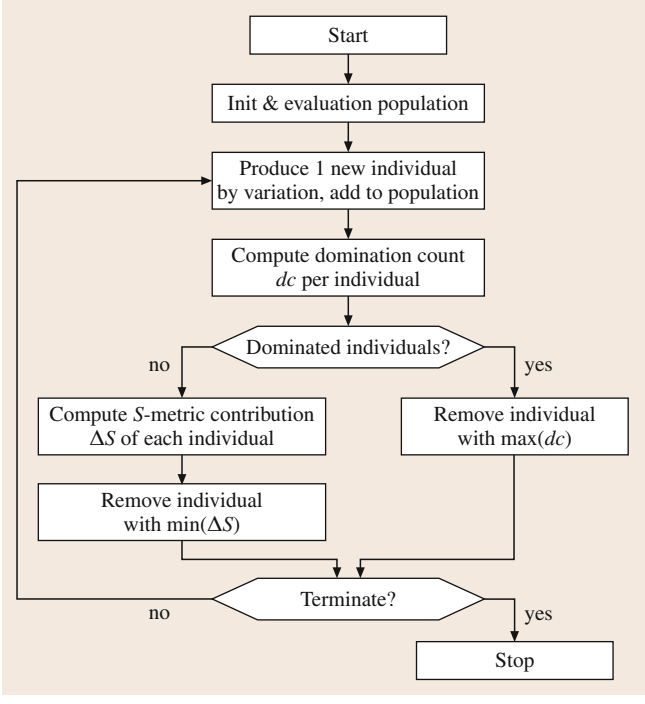

Fig. 58.4 Working scheme of the SMS-EMOA. Termination is done according to predefined conditions, e.g., a certain budget of fitness evaluations

58.3.1 Basics of Multiobjective Optimization

Multi-objective optimization fundamentally relies on Pareto dominance. A point in the objective space of two or more objective functions is dominated, if there is at least one other that is not worse in all objectives and better in at least one (Fig. 58.3a). As the optimization progresses, the population approaches the Pareto front which resembles the set of optimal compromises and consists of non-dominated points only.

Several criteria exist to judge the quality of whole populations within the algorithm run (as means to determine the next search steps) and thereafter to assess optimization success. One of the most popular is the hypervolume, the amount of objective space coverered by the population with regard to a reference point as documented in the right panel of Fig. 58.3.

The *S*-metric selection evolutionary multiobjective algorithm (SMS-EMOA) is a further development of the popular NSGA2 (nondominated sorting genetic algorithm 2) by [58.43]. Figure 58.4 displays its major steps. Starting from a usually randomly placed population, a loop begins with deriving one new individual (search point) and adding it to the population. The domination count of each individual is computed by counting how many other individuals dominate it. If such dominated individuals exist, the one with the largest domination count is deleted. Otherwise, the hypervolume contribution of each individual is determined (Fig. 58.3b), and the individual with the smallest contribution is deleted. If the current state does not fulfill the termination criterion (e.g., a predefined budget of function evaluations) the loop starts over. After terminating, the remaining population is the result set.

58.4 Solving General Phase-Equilibrium Problems

We present the results of phase-equilibrium calculations for the three-component system water/methanol/MMA as well as for the three-phase systems water/MMA and water/furfural. The corresponding optimization problems have four, three, and three decision variables.

PC-SAFT uses statistical mechanics for its simulation of thermodynamic systems and thus requires a calibration of some pure-component parameters and one binary parameter. The aim of this calibration is to achieve a consistency between the calculated phase equilibria and results of physical experiments. Carrying out this task manually for a single substance takes up several days of work for a chemical engineer, although the data of the physical experiments are already available in the literature [58.44]. These data contain series of measurements of temperature, density, and pressure for the vapor and the liquid phase of each substance. Among the several parameters that model the molecular properties, there are five per substance that have to be estimated. These are the number of sphere segments m, the segment diameter σ, the segment energy parameter ϵ/k, an association energy $\epsilon^{\mathrm{AiBi}}/k$, and the effective association volume κ^{AiBi}. Two different association sites are assigned to all the considered substances. If the substance is non-self-associating, then association energy as well as association volume are set to zero. Besides the five (three) parameters per substance, the model requires one parameter k_{ij} that is characteristic for each binary mixture. The respective values for all these parameters were taken from [58.45, 46] and are summarized in Tables 58.2 and 58.3. The applicability of PC-SAFT to model the mentioned systems in good agreement with experimental data has been proved in [58.46].

The following experiments show that the MOAMO approach provides a reliable and fast tool for the detection of equilibrium points which are difficult to find with standard optimization tools as a gradient or quasi-Newton search.

Table 58.2 PC-SAFT pure-component parameters for considered components

Substance	m	σ	ϵ/k	$\epsilon^{\mathrm{AiBi}}/k$	κ^{AiBi}
Water	1.0656	3.0007	366.5121	2500.6706	0.0349
Methyl methacrylate (MMA)	3.0632	3.6238	265.6874	0	0.0349
Methanol	1.5255	3.2300	188.9046	2899.4906	0.0352
Furfural	4.1604	3.0204	270.0700	0	0.0349

Table 58.3 PC-SAFT binary parameters

Binary system	k_{ij}
Water/MMA	0
Water/methanol	−0.05
Water/furfural	−0.006
MMA/methanol	0

58.4.1 Ternary Liquid–Liquid Equilibrium: Water/Methanol/MMA

In Fig. 58.5, the ternary phase diagram of water/methanol/MMA at 50 °C and 1.013 bar with two liquid phases is shown. The calculation of the tie-lines was performed for different fixed concentrations of MMA in one liquid phase (x'_{MMA}), see Table 58.4, at constant temperature and pressure.

Pre-Experimental Planning

The first objective (58.9) is generated from the error values output by PC-SAFT. These refer to the departure from the equilibrium state between every two phases of

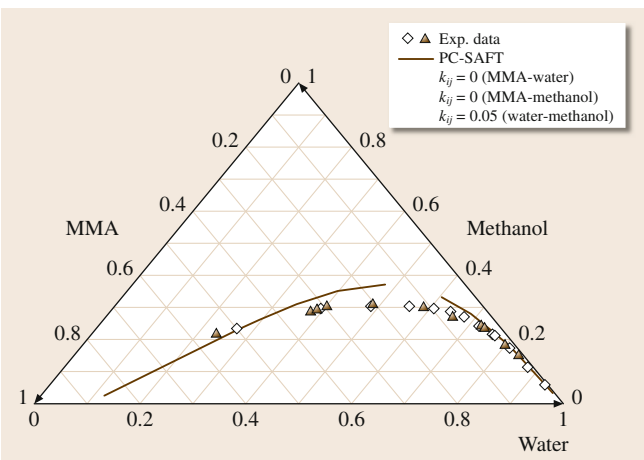

Fig. 58.5 Phase diagram of water/methanol/MMA system at 50 °C and 1.013 bar. The symbols are experimental data from [58.47] and [58.48]. The line is the calculation result of PC-SAFT with MOAMO-approach

one component as given by (58.1).

$$f_1(\boldsymbol{x}', \boldsymbol{x}'') = \sum_{i=1}^{3} |x_i' \varphi_i' - x_i'' \varphi_i''| \,. \tag{58.9}$$

Different formulations of the second objective for the SMS-EMOA were tried and several of them work well. Therefore, a generalization of the distance criterion for the two-component two-phase case in Sect. 58.1 was chosen. It measures the Euclidean norm of a vector of concentration differences (slightly shifted to allow for minimization) and is easily extendable for more components

$$\begin{aligned} f_2(\boldsymbol{x}', \boldsymbol{x}'') &= \sqrt{2} - \|x' - x''\|_2 \\ &= \sqrt{2} - \sqrt{\sum_{i=1}^{3} (x_i' - x_i'')^2} \,. \end{aligned} \tag{58.10}$$

Experimental Task

The task for MOAMO in this experiment is to reliably reach the sought optimum for all indicated MMA concentrations, that is the number of individuals converging to the optimum in the local search phase shall be considerably larger than 1 on average. Furthermore, the MOAMO-based approach shall find the optimum considerably faster than a naïve multistart local search procedure.

Setup

For each of the concentrations indicated in Table 58.4, MOAMO is run five times with 30 individuals in the multiobjective first step. Each search point contained in the last population is then optimized by a local search procedure (CMA-ES is employed for this second step). For each local search, it is recorded if either the undesired trivial solution or the sought optimum is obtained or if the search did not converge. Other than population size and run length (30 and 5000), the SMS-EMOA parameters are chosen as in [58.41].

In order to perform a comparison, the local search procedure (CMA-ES) is started 1000 times for each MMA concentration from a randomized start point and the rate of success for converging to the sought optimum is recorded. The CMA-ES terminates if progress or adapted stepsizes decrease below 10^{-12} as usual.

Table 58.4 MOAMO with 30 individuals, remaining population put into local optimization and rate of success and convergence to trivial solution, averaged over five runs. Where the sum of optimum and trivial is below 30, some local searches did not converge. The last column gives the empirical success probabilities for random start points of the local search

x'_{MMA}	Optimum	Trivial	Success rate (%)
0.05	25.2	3.8	45.0
0.15	0.0	30.0	2.7
0.25	5.8	24.0	3.6
0.35	19.6	10.2	3.9
0.45	25.8	4.0	3.5
0.55	29.4	0.6	2.9
0.65	28.8	0.0	3.1
0.75	29.0	0.6	3.1
0.85	23.2	0.6	2.3

Observations

Table 58.4 comprises the results for the MOAMO approach and in comparison the success rates for the random start local search procedure. Run lengths of the CMA-ES are not given in detail, but mostly range between 2600 and 5000 evaluations.

For the MMA concentrations from 0.25 to 0.85, both methods are consistent: MOAMO obtains the sought optimum from at least 60% of the last population's search points, while the success rates of the random start local search vary between 2 and 4%. However, 0.05 and 0.15 are special cases: In the first case, the problem is obviously not that hard as the random start local search also detects the sought optimum often, and in the second case, the MOAMO approach completely fails.

Discussion

The most striking result of the experiment is that hardness of the problem for the two compared approaches seems uncorrelated. An MMA concentration of 0.05 is much more easily solved by the random start local search than any other, but the success rates for MOAMO do not reflect this. For 0.15, the opposite happens as the problem poses average difficulties for the random start local search procedure, but is very hard for MOAMO. We conjecture that this is an exception as we are almost at the critical point here, where concentrations in both phases differ less and less. Presumably, trivial solution and sought optimum are too equal to separate them in the SMS-EMOA phase via the distance objective. However, we can be satisfied with the results for the other concentrations, where the MOAMO approach reliably detects the sought optimum and is much faster than the random start local search procedure, even if the effort for the first (multiobjective)

phase is considered (which is on the order of one or two local searches).

58.4.2 Three Phase Equilibria: Water/MMA and Water/Furfural

We now turn to an application of the MOAMO approach on 2 component/3 phase systems in order to detect the heteroazeotrope point (a 3-phase equilibrium). The first objective is again obtained from the phase equilibrium equations and differs from the one chosen for the 3 component/2 phase system (58.9) in the number of relevant phase equations. Due to transitivity, four error values remain here. Additionally, a quadratic form is chosen here instead of the absolute value form used in the previous case, under the assumption that the quadratic form simplifies the local optimization task (Quasi-Newton as well as evolutionary optimization methods usually perform better in this case).

$$f_1(\boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') = \sum_{i=1}^{2} \left[(x_i' \varphi_i' - x_i'' \varphi_i'')^2 + (x_i' \varphi_i' - x_i''' \varphi_i''')^2 \right] . \quad (58.11)$$

As for the previous system, it is necessary to determine a suitable second (distance) criterion for the multiobjective first step. However, for three phases, the approach taken in [58.14] has to be generalized in a different way than done for three components. Interestingly, our preliminary test showed that it is sufficient to consider only one component and its three phases to create a distance criterion. We may use mutual phase concentration differences of phases 1 and 2, 2 and 3, and 1 and 3 to aggregate an objective function. (Note that Euclidean distances have been employed in the previous section, however our tests show that for the multiobjective MOAMO step, the choice of the distance norm itself is not very important and Manhattan distances as used here are also sufficient.)

$$f_2(\boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') = 2 - \sum_{i=1}^{2} \left(|x_i' - x_i''| + |x_i'' - x_i'''| + |x_i' - x_i'''| \right) . \quad (58.12)$$

Alternatively, the phase concentration differences can also be stated as three separate criteria, resulting in a four-objective problem for the SMS-EMOA

$$\begin{aligned} f_2(\boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') &= 1 - \sum_{i=1}^{2} |x_i' - x_i''| \\ f_3(\boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') &= 1 - \sum_{i=1}^{2} |x_i'' - x_i'''| \\ f_4(\boldsymbol{x}', \boldsymbol{x}'', \boldsymbol{x}''') &= 1 - \sum_{i=1}^{2} |x_i' - x_i'''| . \end{aligned} \quad (58.13)$$

The following experiment will show whether the aggregated formulation or the separate criteria are more advisable.

The binary system water/MMA in Fig. 58.6 exhibits a heteroazeotrope behavior at 1 bar. According to the phase rule, only one variable can be fixed to determine the heteroazeotrope, as in this case the pressure. The temperature of the heteroazeotrope was found at 81.93 °C and the concentrations of MMA in the three phases were $x'_{\mathrm{MMA}} = 0.841826$, $x''_{\mathrm{MMA}} = 0.488033$, and $x'''_{\mathrm{MMA}} = 0.002577$.

The identification of the heteroazeotrope point for water/furfural at 1 bar was more complicated than the previous system due to the fact that two sought water concentrations are close to each other ($x'_{\mathrm{water}} = 0.911822$ and $x''_{\mathrm{water}} = 0.973374$), see Fig. 58.7. The third water concentration was found at $x'''_{\mathrm{water}} = 0.507017$ and the heteroazeotrope temperature was determined at 97.64 °C.

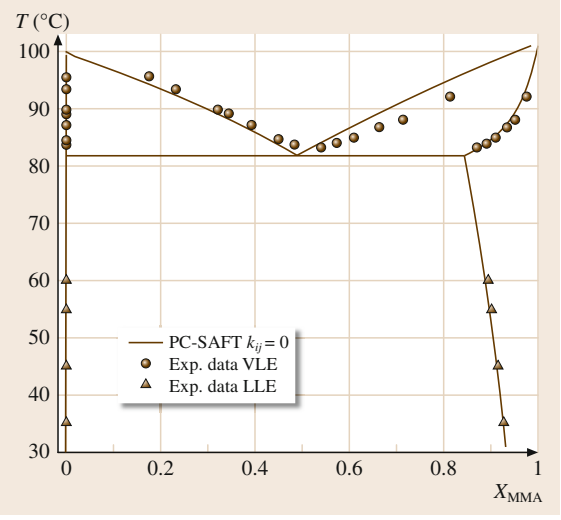

Fig. 58.6 Phase diagram of water/MMA system at 1 bar. The symbols are experimental data from [58.49] and [58.50]. Lines are calculation results of PC-SAFT with MOAMO-approach

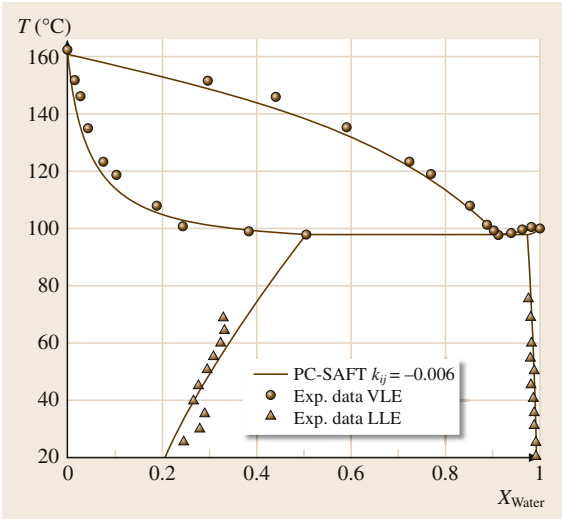

Fig. 58.7 Phase diagram of water/furfural system at 1 bar. The symbols are experimental data from [58.51]. Lines are calculation results of PC-SAFT with MOAMO-approach

Pre-Experimental Planning

Taking over the SMS-EMOA parameters (population size and run length) from the previous experiment led to an unreliable behavior for the two systems tested here. Seemingly, they are more difficult to solve than the given three-component/two-phase system. Therefore, population size is doubled to 60 individuals and run length is accordingly slightly increased to 6000 evaluations.

Experimental Task

As the last paragraph indicated that the problems in this section are even more difficult than the that of Sect. 58.4.1, there is no point in testing against random start local search again. Instead, it shall be determined if the aggregated (58.12) or the separate criteria approach (58.13) is more suitable for solving the problems with MOAMO. To enable a decision between the two, a significant difference in success rates is required.

Setup

For each of the two systems (water/MMA and water/furfural) and each of the problem formulations (aggregated/separate), 30 MOAMO runs are performed and the number of successes is recorded. A run is successful if at least one of the local search steps obtains the sought optimum the number of successful local searches is not recorded. As before, we employ the combination of SMS-EMOA and CMA-ES. The resulting values for the first objective function (computed from the error values output by PC-SAFT) shall be below 10^{-15} in this case, requiring to modify the CMA-ES internal stopping criteria accordingly. Its initial step size is set to 0.01. The SMS-EMOA parameters are set as in the previous experiment except population size and run length which are modified as documented above.

Table 58.5 Success rates for detecting the heteroazeotrope point via MOAMO approach under different formulation of the distance criterion

System	Distance criterion	Success rate (%)
Water/MMA	Aggregated	100.0
	Separate	50.0
Water/furfural	Aggregated	93.3
	Separate	36.7

Observations

The number of successful runs is given in Table 58.5. The aggregated approach seems to consistently perform better than the one with separate criteria, and success rates hint to the fact that the second system poses more difficulty than the first one.

Discussion

Fortunately, the much simpler (aggregated) approach is also the more reliable for both systems. The much larger objective space in the first phase (four instead of two objective functions) obviously outweights the benefits of a *correct mapping* by far. Furthermore, for higher numbers of phases, the number of objectives would grow faster than linear, so that in conclusion, the aggregated approach is much more suitable than the one with separate objective functions.

58.4.3 Obtaining the Phase Diagrams

Once the heteroazeotrope point is detected, a phase diagram of the system may be obtained by systematic exploration of the two-phase equilibria at different temperatures. We simply increase or decrease the temperature (which is a free variable for two-phase systems) by 1 °C and take the solution for the last temperature step as initial point for a local search (executed by the CMA-ES) on every binodal curve. Figures 58.6 and 58.7 have been generated by means of this method. (Note that this is different from the common approach of detecting several two-phase equilibria by means of a quasi-Newton method first and then to conclude on the heteroazeotrope point from these.)

58.5 Conclusions and Outlook

In this chapter, a multistage method named MOAMO (multiobjectivization-assisted multimodal optimization) was presented. It is especially designed for difficult multimodal direct search problems as arising in phase equilibrium detection. However, the method is very well applicable whenever some problem knowledge is available concerning where the global optimum is *not*. The experimental analysis, performed on three different systems with either three components and two phases or two components and three phases, has shown that the approach is reliable and fast. It outperforms random multistart local search by a large margin under nearly all tested conditions. Two important properties of the approach need to be emphasized:

- Unlike many attempts to solve phase-equilibrium problems by means of evolutionary or related algorithms, MOAMO utilizes known features of the problem to direct the search and thereby avoids spending too much effort in repeatedly approaching trivial solutions. However, it does not make any assumptions about the *location* of the sought optima and is thus still a generic approach.
- Unlike in some other multiobjectivization approaches, the second objective is population independent. Moving a single individual does not change the objective function values of any other. This prevents unwanted feedback loops. The optimization focuses on the problem and not on the current population.

Our results indicate the MOAMO approach as remarkably independent of the actual formulation of the second objective. Performance increases or decreases only gradually for alternative objectives, the overall concept remains intact. However, obtaining better guidelines for setting up a matching second objective is an area for future research, as is the comparison with more different algorithms and the adoption for other problems, not necessarily restricted to phase equilibrium detection.

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