ELSEVIER

Chemical Engineering Science 60 (2005) 6607–6621

Chemical Engineering Science

www.elsevier.com/locate/ces

Application of the simplex simulated annealing technique to nonlinear parameter optimization for the SAFT-VR equation of state

B. Behzadi[a], C. Ghotbi[a,*], A. Galindo[b]

[a]*Department of Chemical and Petroleum Engineering, Sharif University of Technology, P.O. Box 11365-9465, Tehran, Iran*
[b]*Department of Chemical Engineering and Chemical Technology, Imperial College London, South Kensington Campus, London SW7 2AZ, UK*

Received 25 December 2004; received in revised form 8 May 2005; accepted 13 May 2005
Available online 14 July 2005

Abstract

A non-equilibrium simplex simulated annealing algorithm is applied as a global optimization method to parameter optimization for an equation of state based on the generalized statistical associating fluid theory incorporating potentials of variable range. The parameters are determined by optimizing the calculated phase behaviour of a number of pure solvents, such as water and alcohols, and aqueous electrolyte solutions. The optimized parameters obtained via the simulated annealing algorithm are compared to those obtained using the simplex method and, for the electrolyte solutions, a gradient-based quasi-Newton method. In the case of the pure solvents, the lowest values of the objective function have been obtained using the simulated annealing technique in six out of the seven studied systems, while for the electrolyte solutions the method results in the lowest values in nine systems out of 11; in the other systems the local methods have resulted in lower values of the objective function. It is observed that both for the solvents and the solutions considered the parameters obtained using the annealing technique are theoretically justifiable, follow physically meaningful trends, and can more easily be generalized; such results provide a measure of confidence that the annealing method does converge to the global minimum in the majority of the studied systems. For pure solvents a simple generalization of parameters leads to accurate predictions for other solvents in the same homologous series. In the case of the electrolyte systems correlations among parameters obtained via simulated annealing can be qualitatively identified, and a simple correlation is proposed which simplifies the molecular models. This is generally not the case for the two local minimization methods considered which, except for a few specific cases, lead to parameters showing no general trends, despite the calculated phase behaviour being almost identical.

Keywords: Nonlinear parameter optimization; Simulated annealing; Simplex method; Gradient-based methods; SAFT-VR; Equation of state; Electrolyte solutions

1. Introduction

The development of molecular models has been an active area of research for more than a century, in great part due to the need for accurate representations and predictions of the physical properties of matter in the design and development of processes in the chemical process industries. In order to achieve this goal, numerous equations of state have been presented, recently the most successful have been those based on detailed molecular models through statistical mechanical approaches (Prausnitz et al., 1999) as they can offer real predictive capabilities. It should be noted, however, that any equation of state ultimately relies on a number of intermolecular parameters which must be obtained by direct comparison with experimental data. The optimum values of these parameters are obtained by fitting the calculations to available experimental data, using a suitable parameter optimization method. An advantage of modern equations over traditional cubic equations of state is that fewer experimental data points may be needed to obtain a full description of the phase behaviour of a system, especially in the case of mixtures. A disadvantage, however, is that, in general,

* Corresponding author: Tel.: +98 21 600 5819; fax: +98 21 602 2853.
E-mail address: ghotbi@sharif.edu (C. Ghotbi).

0009-2509/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2005.05.041

a more sophisticated molecular model will be accompanied by a larger number of parameters to be estimated. Fortunately, in many occasions, physical insight can be used to reduce the parameter set.

Recently attempts have also been made to regress large databases of experimental data using artificial neural networks (Iliuta et al., 2000). Results for vapor liquid equilibrium calculations are promising, especially considering the large amounts of experimental data that are now available. However, since the technique is based on interpolation among experimental data and not on theoretical insight, its capabilities in handling complex systems and predicting conditions outside the range of the data are still to be proven. Furthermore, the method has not yet been applied to more complex phase behavior, such as liquid–liquid and solid–liquid phase equilibrium. Therefore thermodynamic models remain the most popular tools for modeling experimental data, predicting phase equilibrium conditions, and calculation of the physical properties of pure substances and mixtures.

Since thermodynamic models may become highly nonlinear with respect to the parameters, efficient optimization techniques must be used. To this end, many different nonlinear optimization methods have been developed, usually based on minimizing some type of least squares or maximum-likelihood criterion (e.g. Fabries and Renon, 1975; Anderson et al., 1978; Valko and Vajda, 1987; Gau et al., 2000; Vasquez and Whiting, 2000). Gradient based quasi-Newton methods, like the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method (Press et al., 1992), can be readily implemented for this purpose using values of the gradients of the fitting function. The Levenberg–Marquardt (L–M) algorithm (Marquardt, 1963), which combines features of the gradient-based approach with the high convergence rate of analytical expansions of the fitting function, is also commonly used. The algorithm progresses in the direction of the steepest descent, using values of the gradient obtained by summing up contributions from every calculated point. Alternatively, if gradient evaluations are expensive or there are other difficulties (e.g. the occurrence of singularities), non-gradient methods such as the simplex algorithm (Nelder and Mead, 1965) are typically incorporated; in these the optimum is identified by systematic trial and error. Unfortunately a major drawback of all of these methods is that they do not guarantee that the global minimum, i.e., the best set of intermolecular parameters, has been found. In the context of parameter estimation for equations of state the objective functions are rarely convex, almost always presenting multiple local minima. In these problems, optimizers such as those mentioned above have a high tendency of getting 'trapped' in the local minima, especially for inappropriately defined starting points.

Failure to converge to the best local minimum point—or the global minimum—of the objective function has several consequences. Obviously the model used will not provide the highest degree of accuracy, since the best possible set of parameters has not been obtained. In addition, it may limit the capabilities of the model in reproducing specific phase-equilibrium conditions, such as the representation of azeotropic mixtures and liquid–liquid equilibria in partially miscible systems (Gau et al., 2000). In such cases, the model will not only be performing inaccurately, but it would actually be producing physically incorrect results. Finally, in some cases, the physical or mathematical insight which could have been gained through the study of the correlations and trends among different parameters of the model might be obscured. It is therefore necessary to consider the combined use of global minimization algorithms with an appropriate search strategy for model parameter optimization.

Global minimization techniques can be divided as deterministic (e.g. Schnepper and Stadtherr, 1996; Floudas, 2000) and stochastic (e.g. Cardoso et al., 1996). Deterministic methods, which systematically search through specified possible intervals of the parameters, guarantee convergence to the global minimum, but they require advanced programming skills. On the other hand, stochastic methods incorporate random searching techniques relatively simple to implement, and much of the necessary program codes are readily at hand (e.g. from optimization texts (Press et al., 1992)). Stochastic approaches are especially suited to problems introducing large numbers of parameters, or where the objective function moves along numerous relatively flat valleys. Despite the attractive features of these algorithms, their capabilities have not been studied thoroughly in parameter estimation problems for recent thermodynamic models, and many researchers remain skeptical of their performance. As a result, thermodynamic modeling is still widely practiced using local optimization techniques (e.g. Fabries and Renon, 1975; Anderson et al., 1978; Valko and Vajda, 1987; Gmehling et al., 1977–1990).

In this work, parameter optimization for the statistical associating fluid theory (SAFT) (Chapman et al., 1989, 1990), a sophisticated multi-parameter equation of state, has been carried out using a simulated annealing technique (Press et al., 1992), which is a stochastic global optimization method. The results, where appropriate, have been compared to those obtained using the simplex (Press et al.,1992) and BFGS (Press et al., 1992) methods which, as mentioned before, are local optimization methods. The model has been applied to study the fluid phase behaviour of systems including pure solvents (water and alcohols) and aqueous electrolyte solutions.

2. Optimization methods

The Metropolis algorithm (Metropolis et al., 1953) was first applied to combinatorial minimization problems by Kirkpatrick et al. (1983) and Kirkpatrick (1984). It was later applied to the optimization of multimodal continuous spaces (e.g. Press and Teukolsky, 1991), and has been considered