Optimization of Equations of State using the Direct Search Method

Renee J. Perez
Marcelo Epstein
University of Calgary, Mechanical Engineering Department, Calgary Alberta, Canada

The biggest problem that arises in the thermodynamic modeling of the phase equilibrium of liquid or gaseous hydrocarbons is the predictability of the equations of state. Both the virial and the cubic Vander Wals equations of state require a big amount of unknown parameters to reproduce experimental data. These parameters are usually adjusted manually, by trial and error methods, or by methods of Newton-Rapshon. In this paper we present an alternative method to the regression process and adjustment of parameters within the equations of state that does not require partial derivatives and is mainly based on a direct iterative search, within a finite mesh, and through interpolation of an objective function, to find a local minimum.

Optimization methods for direct search (DS) were first used in the 1950s but fell into disuse some twenty years later, probably due to the slow convergence and lack of theorems which demonstrate that the algorithms actually converge to a minimum. Twenty years later, in the 1990s, the interest in these methods awoke again within the mathematical community. Among the advantages offered by these methods, we can mention the following: (1) Methods of DS require only continuity (not differentiability) of the objective function, (2) restrictions of all kinds are easy to implement, (3) although the method does not converge to a minimum, its progress is such that the sequence of values of the objective function at the points considered is always monotonically decreasing (in other words, the method may not converge, but never really diverges).

The simplest DS method is the so-called *compass method* used in this work for optimizing equations of state and reproducibility of expansion data. In principle the method works as follows: in a domain of n dimensions, meshing with an orthogonal equidistant grid, each point inside the domain has exactly $2n$ nearest neighbors. In two dimensions these neighbors can be called north, south, east and west, which justifies the method name of compass. In a border point, some of these neighbors do not exist. In any case, we call feasible neighbors all those who are within the domain or in the boundary.

The maximum possible amount of neighbors is clearly 2n. Once the objective function, which is the equation of state thermodynamic property, has been calculated in one point and in its feasible neighbors, there are only two possibilities: (a) the value of the function or property at the point under consideration is less than or equal to each of its neighbors feasible; (b) the value of the function in one of the feasible neighbors is less than at the point in question. In the case of (b) we simply move to the feasible neighbor with the minimum value of the objective function (in case there are two neighbors with the same value, the choice is arbitrary). In the case of (a), we remain at the point in question, but redefine the mesh subdividing it in half. The process continues until we have reached a satisfactorily low value of the objective function or until we have reached a sufficiently fine mesh function. The simplicity of the algorithm is impressive. And it works.