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Korean J. of Chem. Eng., 3(1) (1986) *77 – 81*

REGRESSION OF CONSTRAINED PARAMETERS FOR NONLINEAR THERMODYNAMIC MODELS

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(*Received 14 November 1985 • accepted 14 January 1986*)

Abstract—An algorithm based on variable Metric method has been applied to the determination of molecular thermodynamic model parameters from experimental data when any model need several constraints. Implementation of the method is illustrated in the reduction of multi-property equation of state data for the systems of argon, nitrogen and methane.

INTRODUCTION

Recently reliable and robust nonliner programing techniques have become available for optimizing functions subject to equality and/or inequality constraints. Such numerical techniques can be useful tools in the field of molecular theromodynamics as well as other chemical engineering fields.

One such technique is the variable metric method of Powell [1,2]. This algorithm has been applied to the problem of estimating parameters in a nonlinear critical point constrained multiproperty equation of state. The important feature of this technique is that an optimum set of parameters can be obtained which at the same time fit exactly constraints imposed by thermodynamic considerations. With an equation of state the constraints are those implied by the gas-liquid critical points. Although the method is used here with the new equation of state developed by Yoo [3], it may be used with any type of complex molecular thermodynamic models.

CONSTRAINED OPTIMIZATION BY VARIABLE METRIC METHOD

The estimation of parameters in any type of problem reduces one which an objective function $F(\underline{x}) = F(x_1, x_2, \ldots, x_n)$ is to be minimized by obtaining optimum values of the n adjustable parameters $\underline{x}$. In addition, the parameters in the model may be subject to both equality and inequality constraints given by

$$C_i(\underline{x}) = 0, \quad i = 1, 2, \cdots, m' \qquad (1)$$
$$C_i(\underline{x}) \leq 0, \quad i = m' + 1, \cdots, m$$

where m′ is the number of equality constraints and m is the total number of both equality and inequality constraints on the values of the variables. Here we are concerned with the case $F(\underline{x})$ and $C_i(\underline{x})$ are differentiable and suppose that all first and second derivatives can be calculate for any $\underline{x}$.

Among various methods proposed on constrained optimization such as penalty function method [4], augmented Lagrangian method and superlinear constraints approximations [1, 2, 5, 6], the Powell's algorithm based on variable metric with superlinear approximation is especially advantageous when an objective function need a large number of both equality and/or inequality side conditions with high nonlinearity of objective and constraint functions.

A detailed discussion of Powell's algorithm is inappropriate here. Instead, only the fundamental concepts are introduced to provide a qualitative understanding. Interested readers are referred to the works of Powell [1, 2, 6] for complete description and implementation of the method. The variable metric methods have been used successfully for many years for unconstrained optimization calculations. A good survery of their properties is given by Dennis and More [7]. The algorithm of Powell for solving the general constrained optimization problem combines the advantages of variable metric methods for unconstrained optimization calculation with the fast convergence of Newton's method for solving nonlinear equations. It is based on the works of Biggs [8], Han [5, 9], and Powell [6].

With the Powell algorithm the derivatives of the objective function yields the gradient of $F(\underline{x})$ and is defined as $G(\underline{x})$. Similarly, the derivatives of all the constraints give a matrix, K, whose columns are the normals of the constraints. Both the gradient vector and normal matrix are required in the algorithm.

The first iteration starts with an initial estimate of $\underline{x}$ at which the gradient and normals are evaluated. A positive definite matrix, B*, defined as the current "metric," is initialized to the identity matrix. In an unconstrained optimization B* is regarded as an approximation to the second partial derivatives. As discussed by Powell, in a constrained optimization the matrix B* may not be strictly identified in this way. However, the algorithm provides a method for updating the matrix B* such that it includes some second derivatives information, and thus, provides superlinear convergence.

Based on the current values of the object function and its gradient and on the current matrix, a search direction vector, $\underline{d}$, is calculated which satisfy the constraints and minimize a guadratic function, with the search direction vector the parameters are updated as in the unconstrained optimization problem. Then matrix B* is revised and other iteration is begun. Convergence is assumed when no further improvement is achieved in minimizing the objective function.

PERTURBED HARD-CORE EQUATION OF STATE

While it is not yet possible to construct a rigorous statistical-mechanical theory of fluids, much progress has been made developing approximate models based on the radial distribution function and the interparticle potential function for gases and liquids.

Among numerous theoretical models, one of the most simple and attractive are the hard-core equation of state. The principal advantage to these equations are that the fundamental integral equation based on radial distribution function can be solved analytically when using hardcore potential.

This equation has been discussed previously by several authors [10-12]. However, becaus of its simplistic nature, only limited success in representing properties of real fluids has been achieved, and difficulties are often experienced in qualitatively representing properties near the critical point and the molecular rigidity at extreme pressure region.

In an attempt to obtain an equation of state with improved accuracy for engineering-oriented calculations, a new hard-core equation of state have been considered by the author[3] based on molecular geometric consideration for the reference repulsive terms and weakly perturbed attractive terms.

Here we summarized several features of this equation and illustrate how the Powell algorithm can be used to determine its adjustable parameters to achieve a reliable representation of the experimental data. This modified equation of state can predict over very wide range of fluid phase properties including those in the critical region providing the experimental data and the critical point constraints are correctly utilized.

The expression for the compressibility factor is the sum of a refenence, hard-core terms and a perturbed attractive terms:

$$Z = Z_{reference} + \sum_{k} \lambda^{k} Z_{perturbed}, \quad (\lambda^{k} > 0) \tag{2}$$

$$Z_{reference} = \frac{1}{(1-h)} + \frac{G_1 h}{(1-h)^2} + \frac{G_2 h}{(1-h)^3} + \frac{G_3 h}{(1-h)^3} \tag{3}$$

$$Z_{perturbed} = \frac{G_o \Phi h}{RT} (B_1 + B_2 h + B_3 h^2) \tag{4}$$

$$h = G_o / V = G_o \rho \tag{5}$$

In equatin (3) G_0 is the effective hard-core volume and G_i ($i=1, 2, 3$) are the geometric coefficients in the reference potential, where the hard-core volume G_0 can be separately related as functions of molecular weight, density at melting point and system temperature [13]. However, in this illustration we treat as adjustable parameters since this crude assumption increase model nonlinearity significantly in the optimization. In principle, also the coefficients G_i in the reference potential can be related before perturbation as shape factor parameters by considering the molecular characteristics such as hard-disk, hard-dumbell, or spherocylinder. In equation (4) the coefficients B_j($j=1,2,3$) are the first order perturbation constants. These coefficients of G_i and B_j are then strongly related to the bulkiness of different compounds and they may be correlated with factors such as molecular bulkiness. Currently this theoretical approach is investigating by the author. Φ is the attractive energy (here the Lennard-Jones kinetic energy for molecularly simple systems). In the present illustrative study we treat all coefficients as adjustable parameters although any dispute is indispensable, $x_1=G_0$, $x_2=G_1$, $x_3=G_2$, $x_4=G_3$ and $x_5=B_1$, $X_6=B_2$, $x_7=B_3$, respectively. Here the objective function was expressed by the sum qf two contributions: the sum of all the squared, weighted deviations in the calculated pressure (PVT) and in the calculated vapor pressure (PV).

$$F(\underline{x}) = W_{pvt} \sum_{j}^{N} (P^{c} - P^{e})_j^2 + W_{pv} \sum_{i}^{N'} (P_{sat}^{c} - P_{sat}^{e})_j^2 \tag{6}$$

In equation (6), W is a weighting factor and N is the number of data points. The superscript c indicates a calcluated value, given by the equation of state, and the superscript e indicates an expermental value. In fitting equations of state, we considered equality constraints; those given by the critical point conditions.

$$C_1 = (P^{c} - P^{e})_{T_c, V_c} = 0 \tag{7}$$

$$C_2 = \left(\frac{\partial P}{\partial V}\right)_{T_c, V_c} = 0 \tag{8}$$

$$C_3 = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c, v_c} = 0 \tag{9}$$

In the present study these three critical point zero constraints are assumed to be satisfied in the program within the tolerance of near-zero values.

RESULTS AND DISCUSSION

To provide the proper search direction, good initial parameter estimates are required in the algorithm. They were obtained by first performing linear regression of all the parameters except the hard-core volume parameter, G_0, which was set as a unique physical constant for different components. The hard-core volume parameter is directly related to the hard-sphere diameters. Only PVT data were used in the linear regression by common least square subroutine. All the parameters were then adjusted with the powell algorithm. A typical iteration is shown in Figure 1 and 2 for pure argon; the values of the objective function and constraints are plotted with respect to the number of iteration. In the initial stages, there are large changes in the magnitude of the objective function since the introduction of constraints tend to increase the deviation of squared sum and the search direction vector start adjust simultaneously both functions to satisfy the optimization scheme. However, once the constraints are satisfied, the algorithm converges rapidly and yield a very small value for the overall sum of squared residuals. Convergence is achieved when the equation $|F(\underline{x}) - F^*| + |\Sigma \alpha_i C_i(\underline{x})|$ is less than the convergence tolerance of 1E-06. Here F^* is the predicted final value of the objective function, and α_i is the Lagrange parameter at the solution of the most recent quadratic programming calculation.

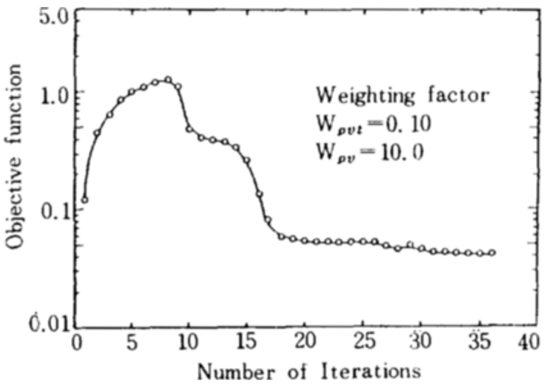

Fig. 1. Minimization of objective function by variable metric method for pure argon.

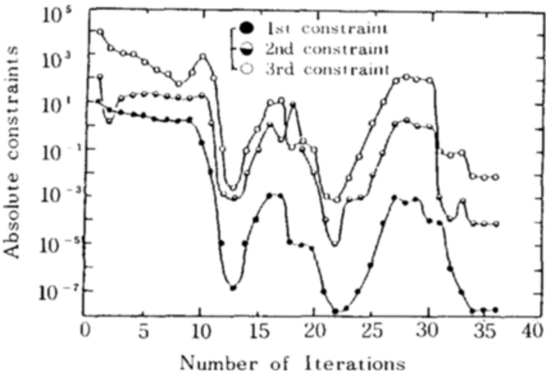

Fig. 2. Optimization of constraint functions by variable metric method for pure argon.

The weighting factors for the systems were set at $W_{pvt} = 0.1$ and $W_{pv} = 10.0$ for PVT data and vapor pressure data respectly. The heavier weighting for the vapor pressure data increases that good vapor pressures are obtained. The illustrative optimum values of parameters and constraints are given in Table 1 and 2 for systems argon, nitrogen and methane. The optimum

Table 1. Minimized values of critical point constraints using the variable metric method for illustrative systems.

System	Critical point constraints		
	$(P^c - P^e)_{T_c, v_c}$	$\left(\frac{\partial P}{\partial V}\right)_{T_c, v_c}$	$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c, v_c}$
Argon	-0.383×10^{-8}	0.4352×10^{-5}	0.1662×10^{-3}
Nitrogen	0.160×10^{-9}	0.6125×10^{-4}	0.1324×10^{-1}
Methane	0.123×10^{-5}	0.345×10^{-3}	-0.101×10^{-1}

Table 2. Calculated pure component parameters for illustrative systems.

system	Iteration Number	Constraint optimized value						
		G_0	G_1	G_2	G_3	B_1	B_2	B_3
Argon	36	0. 01173	3. 7283	- 9. 6685	25. 0319	1. 3714	- 3. 6586	7. 7999
Nitrogen	19	0. 0110	5. 1108	-13. 8032	46. 1221	2. 4108	- 7. 9026	20. 4825
Methane	162	0. 006298	11. 2857	-18. 8608	33. 8615	3. 4044	-17. 7899	58. 5145

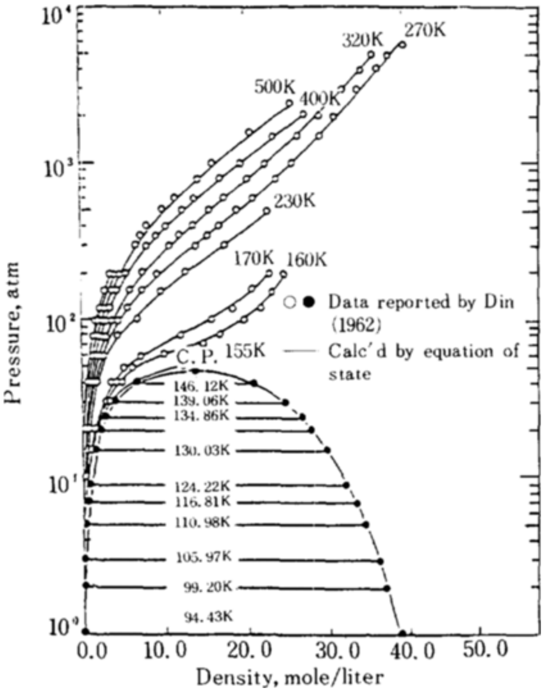

Fig. 3. **Comparison of calculated and experimental densities for pure argon.**

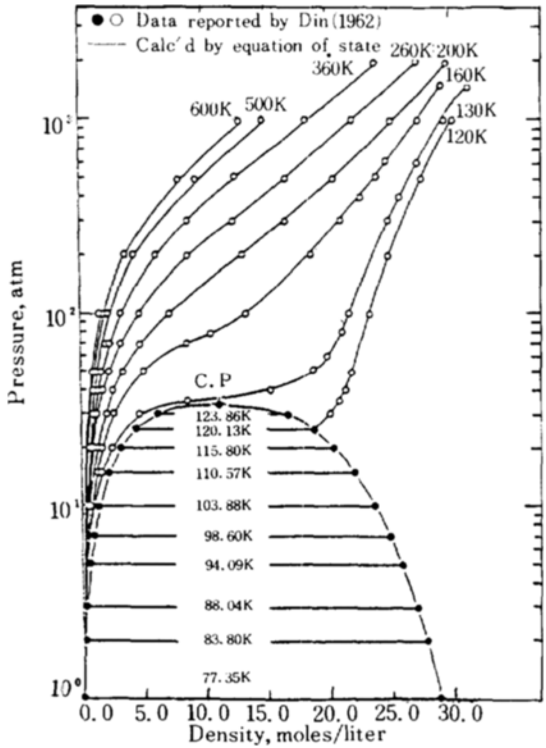

Fig. 4. **Comparison of calculated and experimental densities for pure nitrogen.**

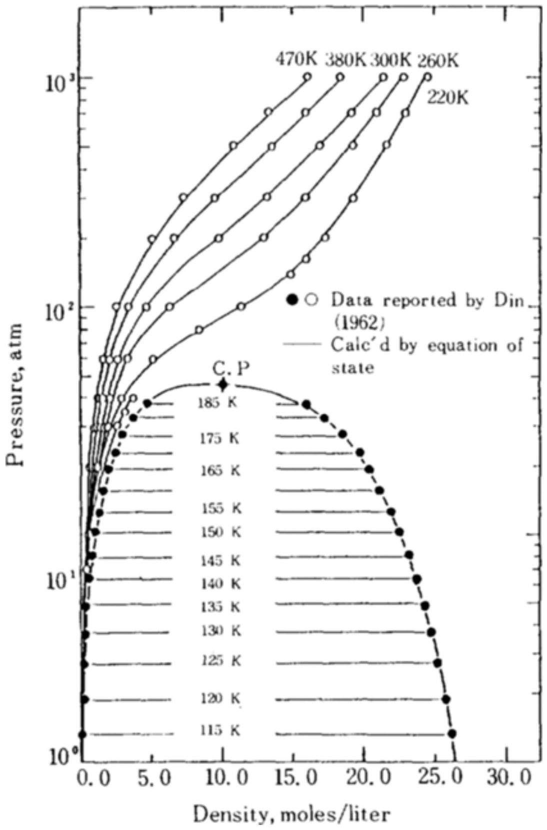

Fig. 5. **Comparison of calculated and experimental vapor pressures for pure methane.**

values of constraints are not exactly zero as we defined previously, however, those values are sufficiently near zero to satisfy the zero constraint conditions. A very good representation of the critical region including critical point are achieved.

The calculated densities for argon, nitrogen, and methane are shown in Figure 3-5. Experimental data [14] for pressure up to 5,000 atm, and temperature to 600 K.

Figure 6 shows calculated and experimental vapor pressure for the same systems; the calculated values agree almost exactly over the entire range.

CONCLUSIONS

We have shown how a constrained nonlinear programming technique of Powell can be applied to the problem of estimating constrained parameters in a tentative multi-property equation of state.

The technique presented here is especially useful for determining parameters in highly complex thermodynamic model as well as other equations which re-

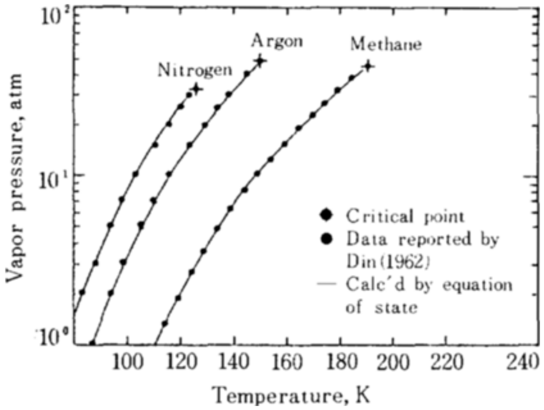

Fig. 6. Comparison of calculated and experimental vapor pressures.

quire that several constraints imposed by the thermodyanmic considerations also must be tatisfied.

ACKNOWLEDGEMENTS

The author is grateful to professor Thomas F, Anderson, at the University of Connecticut, for his helpful discussions.

NOMENCLATURE

B* : Positive definite materix in Powell algorithm
Bi : Perturbation constants
Ci : Constraint functions
d : Vector that minimize the objective function
F : Objective function
G : Geometric expansion coefficients
g : Gradient of objective function
h : Density parameter
K : Metrix of constraints normal
N : Data points
p : Pressure, atm
Q : Quadratic function
R : Gas constant
T : Temperature, K
V : Volume, liter/mole
W : Weighting factor
x : Vector of parameters
Z : Compressibility factor

Greeks Letters

α : Lagrange parameter
Φ : Lennard-Jones kinetic energy
λ : Perturbation constants
ρ : Density

Superscripts

c : Calculated
e : Experimental

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