Computational Aspects of Equations of State: Fact and Fiction

A detailed study has been made of the computing times for several common equations of state used by industry. The cubic equations are approximately equivalent to more complicated equations (e.g., perturbed hard chain and BWRS) for systems with eight or more components. Thus, it is not justified to choose cubic equations over other forms purely on the basis of computational advantage. Further, the study identifies mixing-rule summations as the dominant consumer of computing time.

P. M. Mathias, M. S. Benson
Air Products and Chemicals, Inc.
Allentown, PA 18105

Introduction

It may seem anachronistic to be concerned about computational time in this age of superfast computers. But there are several factors that make a study of the computer times of equation of state models both timely and useful:

- There are several misconceptions concerning equation of state computer time.
- There are many applications where the computation burden of even simple equations of state is excessive.
- A detailed study of this kind has not been reported before.

We made the decision to undertake the present study as a result of the discussion at the Symposium in Memory and Appreciation of Otto Redlich that was held at the 1984 Annual AIChE meeting in San Francisco. There appeared to be widespread belief that the cubic equations (e.g., Soave, 1972; Peng and Robinson, 1976) are far more computationally efficient than other, more complicated models, and that this results mainly because the cubic equations have the advantage of an analytical solution for the density root. The same belief is in evidence at most symposiums on chemical engineering thermodynamics. Our study shows this perception is not true.

Even though today's computers are very powerful and the computers of tomorrow promise to deliver far greater number-crunching capabilities, there is a real need to reduce the expense of computing thermophysical properties while retaining the desirable accuracy. Sophisticated thermophysical models are routinely used in steady state simulations, which has resulted in reliable and accurate, yet inexpensive, designs. But even large mainframes do not provide an infinite and cost-free computing resource, and thus there is still a practical limit to the size and complexity of flowsheets that can be simulated. In addition, the simulation activity is moving to smaller and slower machines. Finally, there are applications like dynamic simulation and reservoir modeling where even relatively simple thermophysical models cause excessive computational requirements. Thus, there is good reason to analyze computer times of equation of state models.

A detailed study of this kind has not been reported in the literature. Boston and Mathias (1980) presented the results of a small timing study that is in agreement with the main conclusions of our investigation. However, the Boston-Mathias study was a minor item in a broad paper and may have been overlooked by many researchers.

Approach to Timing Study

The CPU time of computerized models varies in a complex and interrelated way with hardware and software. It is therefore impossible to design a study that will lead to a definitive determination of the computer time consumption of various equation of state models. It is also unnecessary to do so since we need only be concerned with those characteristics that cause large changes (increases or decreases) in CPU time. The goal of this investigation has been to determine approximately the relative computer times of various equation of state models and identify those parts that consume the dominant portion of the CPU time.

We have eliminated some of the ambiguity arising from software differences by using several equations of state from the widely available public version of the ASPEN simulator. It is also important to evaluate the impact of mixing rules on CPU time. Therefore, we have evaluated four Peng-Robinson (PR) variants with increasingly complex mixing rules. All CPU times reported in this study are for the IBM 3081 computer at Air Products and Chemicals, Inc. This approach permits approximate but realistic evaluation of the total CPU time required for process calculations (e.g., distillation program), but it should be emphasized that we are mainly concerned with relative CPU times.

In order to analyze the results of the timing study it is useful to have available the relative CPU times of the various common functions (multiplication, square root, logarithm, etc.). These are presented in Table 1, where the CPU time relative to multiplication is shown. Division takes about twice the CPU time required for multiplication. Functions such as square root and exponential, which require approximations to infinite series, have a relative value of 12–15. Finally, raising a number to a real power, which requires two infinite series evaluations (logarithm and exponential), has a relative value of about 32. These results are only qualitative and could change as a result of new computer technology; yet Table 1 allows an approximate assessment of the computational load of alternate mathematical formulations of thermophysical models.

Density Root Calculation

Thermodynamic property computations using equations of state (EOS) first require computation of the density root. Fugacity coefficients and enthalpy and entropy departure calculations follow only after the density computation. One common misconception has been that the density root calculation contributes the dominant fraction of the time for derived property calculations. As part of the timing study, CPU times for 10,000 density calculations for the cubic PR equation of state were measured. The pressure was varied to give results in both the one- and the three-root regions. Comparison was also made between an analytic root solution and a numerical strategy developed for the ASPEN process simulator (Mathias et al., 1984). The analytic solution of the cubic EOS for the case where three roots existed took approximately 0.15 ms/density calculation; for the case where only one root existed, the CPU time was 0.13 ms/density calculation. For both the one- and the three-root regions, the numerical strategy took approximately 50% more time for the computation. The trade-off is between computational efficiency and robustness of the density-root calculation in regions where an appropriate density root does not exist. More important, as we show in the next section, the time for the density calculation is only a small fraction of the total time required for calculation of thermophysical properties.

Comparison of Equations of State and Mixing Rules

The timing study was done by performing a particular calculation many times in order to attain a reliable average. Further, a representative average was obtained by making calculations over a range of conditions: temperature, pressure, and phase (V/L). The results are reported as average CPU time vs. number of components in the mixture.

Table 1. Relative CPU Time for Various Common Functions

	Function	Relative CPU Time
Multiplication	$X*Y$	1
Division	X/Y	2
Square Root	SQRT(X)	12
Power	$X**Y$	32
Exponential	EXP(X)	15
Logarithm	ALOG(X)	13

In order to allow other investigators to reproduce (to a reasonable extent) and analyze our timing study, we have used software taken from the public version of ASPEN for the first part of our study. We studied the following six equation of state models:

1. RK, Redlich and Kwong (1949)
2. RKS, Soave (1972)
3. PR, Peng and Robinson (1976)
4. PHC, Perturbed hard chain (nonpolar version), Gmehling et al. (1979)
5. BWRS, A representative generalized BWR (Benedict, Webb, Rubin) equation, Lee et al. (1979).
6. HOC, Second virial coefficient correlation, Hayden and O'Connell (1975).

The equations for the six equations of state studied are not given here since they are easily accessible in the references cited.

The average CPU times for a single calculation of fugacity coefficients for various n-component systems are presented in Figure 1. RKS and PR are shown together since the results for these two models are virtually identical. In the case of a pure component, the cubic equations (RK, RKS, and PR) are clearly more computationally rapid than the more complicated models (PHC and BWRS), but the difference becomes small for systems with many components. The second virial coefficient model (HOC) is by far the most rapid for a one-component system, but quickly becomes the most computationally intensive for systems with many components; this is mainly because of the exponential terms in the equations for the cross second virial coefficients. The simple RK equation shows only a small increase in computer time as the number of components increases.

It is evident that for a typical system encountered in engineering calculations (six to ten components) the computational time is dependent primarily on the terms involving pairs of components (mixing-rule summations). Thus, the RK equation, which does not require binary summations, is the most computationally rapid. More important, the time spent on the density root iteration is minor and therefore of little consequence.

The PHC model used in this study is the nonpolar version that does not invoke dimerization reactions to describe the properties of polar fluids. When the equations for chemical equilibrium

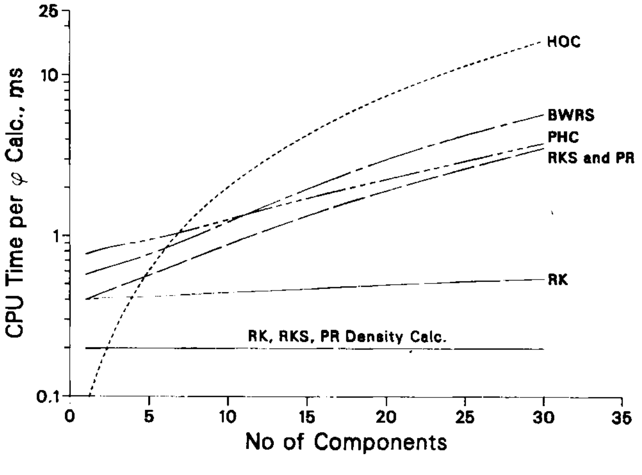

Figure 1. Average CPU time of equation of state models for single calculation of fugacity coefficients.

must be solved, the computational time increases very steeply, as has been shown by Boston and Mathias (1980).

It is illuminating to examine the results of a similar study that calculates enthalpy departures in addition to the fugacity coefficients. These results are presented in Figure 2. The CPU times for RK, PHC, and BWRS remain virtually unchanged, but the times for RKS and PR increase significantly. The latter models are now more computationally intensive than the more complex models for systems containing more than eight to ten components. This apparently anomalous result follows simply because the PR and RKS models, by the nature of their mixing rules, require additional binary summations for the calculations of enthalpy departures, while the models RK, PHC, and BWRS do not.

The second part of the study compares four variants of the Peng-Robinson equation, with increasing complexity in the mixing rules:

1. PR-1, One interaction parameter
2. PR-2, Two interaction parameters
3. PR-TLC, Two interaction parameters and truncated local-composition theory (Mathias and Copeman, 1983)
4. PR-FLC, Two interaction parameters and full local-composition theory (Mathias and Copeman, 1983)

The results of the second part of the timing study are presented in Figure 3. It is evident that the apparently simple introduction of a second binary parameter causes a significant increase in computer time; for example, PR-2 is 50% slower than PR-1 for a 15-component system. The truncated local-composition theory (PR-TLC) causes further increases in computational expense, while the full local-composition model is dramatically more expensive in computer time. PR-FLC is extremely slow because the mixing rules are density-dependent and therefore the expensive binary summations must be repeated during each iteration for the density root.

Conclusions

The timing study described herein is subject to uncertainties, but clearly shows that for typical engineering applications (six to ten components), most of the CPU time is spent in calculating mixing-rule summations. Thus, the CPU time for the density root iteration is minor and consequently the complexity of the pure-fluid equation of state has relatively small effect upon the total computational time. The conclusion is important because it follows that computational considerations do not dictate the use of cubic equations for what are considered to be practical engineering applications. In our opinion, the perception that industry will only accept cubic equations—or at least algebraically simple models—has hindered progress toward the development of effective models based upon statistical mechanics.

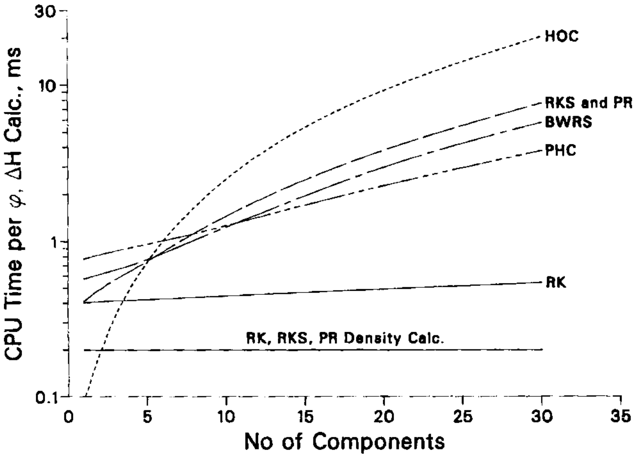

Figure 2. Average CPU time of equation of state models for single calculation of fugacity coefficients and enthalpy departure.

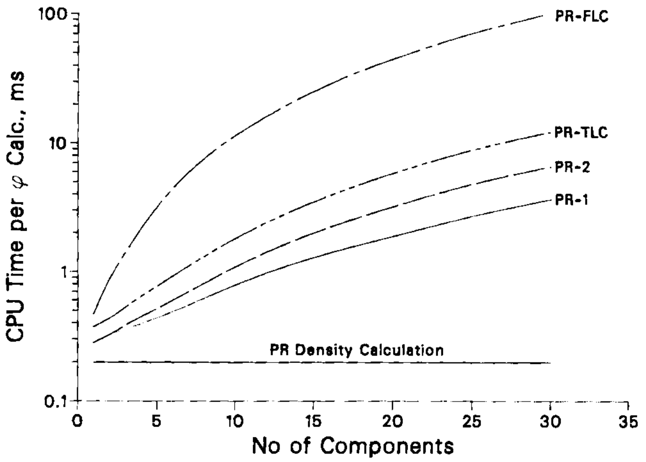

Figure 3. Average CPU time of Peng-Robinson variants, single calculation of fugacity coefficients.

An important fact is that the simple cubic equations work very well (Tsonopoulos and Heidman, 1986). Industry will not and should not replace them with more sophisticated but less accurate and less reliable models whose only strength is their link to theory. We hope that our study will eliminate the tendency to reject sophisticated models because of their erroneously assumed enormous CPU time requirements.

All the models used in this study (with the possible exception of PR-FLC) are well within the computational capability of current computers, when used for steady state process simulation. Further, additional computational expense can probably be tolerated on the basis of increased accuracy. But the CPU time can quickly become excessive for dynamic simulation or if the simulations are run on smaller, and slower, machines.

Finally, this work has identified the mixing-rule summations as an important consideration when coding computationally efficient models or when developing new mixture models for industrial use.

Literature Cited

Boston, J. F., and P. M. Mathias, "Phase Equilibria in a Third-Generation Process Simulator," Phase Equilibria and Fluid Properties in the Chemical Process Industries, Berlin (Mar., 1980).

Gmehling, J., D. D. Liu, and J. M. Prausnitz, "High-Pressure Vapor-Liquid Equilibria for Mixtures Containing One or More Polar Components," *Chem. Eng. Sci.*, **34**, 951 (1979).

Hayden, J. G., and J. P. O'Connell, "A Generalized Method for Predicting Second Virial Coefficients," *Ind. Eng. Chem. Process Des. Dev.*, **14**(3), 209 (1975).

Lee, T. J., L. L. Lee, and K. E. Starling, "Three-Parameter, Corresponding-States Conformal Solution Mixing Rules for Mixtures of Heavy and Light Hydrocarbons," *Equations of State in Engineering and Research*, K. C. Chao and R. L. Robinson, Jr., eds., Adv. in Chem. Ser. **182**, Am. Chem. Soc., Washington, DC, 125 (1979).

Mathias, P. M., J. F. Boston and S. Watanasiri, "Effective Utilization of Equations of State for Thermodynamic Properties in Process Simulation," *AIChE J.*, **30**(2), 182 (1984).

Mathias, P. M., and T. W. Copeman, "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of Various Forms of the Local Composition Concept," *Fluid Phase Equilibria*, **13**, 91 (1983).

Peng, D. Y., and D. B. Robinson, "A New Two-Constant Equation of State," *Ind. Eng. Chem. Fundam.*, **15**(1), 59 (1976).

Redlich, O., and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).

Soave, G., "Equilibrium Constants from a Modified Peng-Robinson Equation of State," *Chem. Eng. Sci.*, **27**, 1197 (1972).

Tsonopoulos, C., and J. L. Heidman, "High-Pressure Vapor-Liquid Equilibria with Cubic Equations of State," 4th Int. Conf. Fluid Properties Phase Equilibria for Chem. Process Design, Helsignor, Denmark (May, 1986).

Manuscript received Jan. 1, 1986, and revision received April 21, 1986.