

Performance improvement on dynamic simulation for high pressure polyethylene synthesis by PC-SAFT

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Abstract

High pressure polyethylene synthesis process requires advanced thermodynamic models such as PC-SAFT, which can be challenging to satisfy both computational reliability and performance. In this work, two new computational techniques were developed and were applied in our customer's projects. The first one is to improve the reliability by identifying a unique tangent point of the equation of state (EOS). The second one is to extend the squeeze theorem to functionals for performance improvement.

Keywords

Vapor-liquid equilibria, polyethylene synthesis, PC-SAFT

1. Introduction

Dynamic simulation requires both accuracy and performance. For modeling accuracy in high-pressure polyethylene process (HPPP), thermodynamic model such as PC-SAFT provides high quality in modeling accuracy, but the performance can be an issue. Two computational techniques were developed and applied to dynamic simulation on HPPP by PC-SAFT with success. The first one is to identify a unique tangent point along the pressure density curve of PC-SAFT equation of state, from which the vapor and liquid density roots can be reliably distinguished. The second one is to extend the squeeze theorem into functionals and approximate the VLE solution with functional extrapolation. Both techniques are generally applicable to any equation of state.

2. Theory

2.1. A unique tangent point on the Pressure density curve

Any equation of state can be described as a pressure density curve, where a unique tangent point (ρ_{tg}, P_{tg}) can be solved by equation 1.

$$\frac{\partial P}{\partial \rho} - \frac{P}{\rho} = 0 \quad (1)$$

Solution of equation (1) can be visualized as a point that a line started from the origin and tangent to the pressure density curve, which is shown on figure 1.

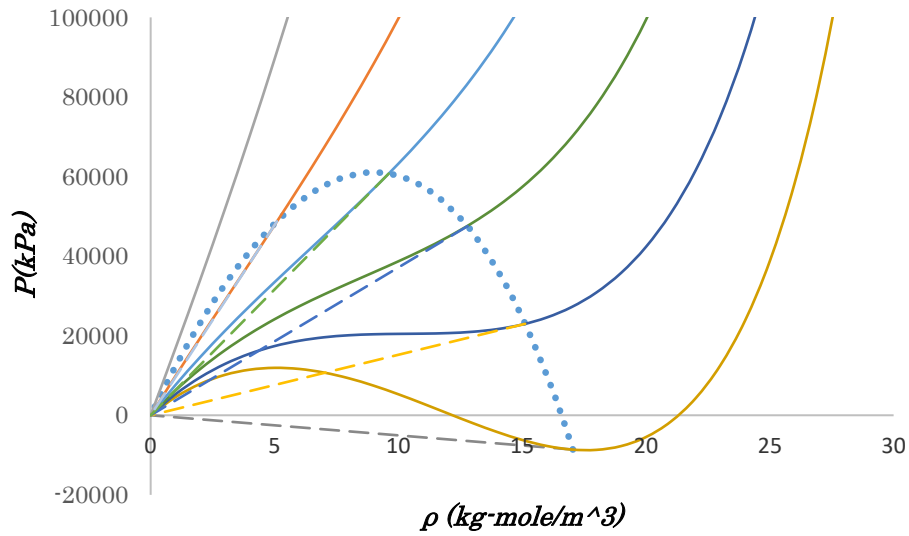


Fig. 1. Solid curves are the equation of state P - ρ curves. As temperature rise, the P - ρ curves would eventually lose the curvature and become a straight line. The dashed lines are the tangent lines at each temperature starting from the origin and tangents to the P - ρ curve at the tangent point. Such tangent point on each P - ρ curve is unique and follows the dotted trajectory as temperature rise. Such phenomenon is generally applied to all equation of states.

As can be seen from figure 1, that the tangent point is unique at each temperature (under given component composition). A liquid phase density root, ρ_{Liq} , at system temperature and pressure would be greater than the tangent point density, ρ_{tg} . A vapor phase density would be less than the tangent point density at relatively low temperature. At high temperature, the vapor phase density root can be greater than the tangent point density value with help from pseudo density root, but that is beyond the scope of this paper. Nevertheless, for low and middle temperature, the tangent point provides a guidance to distinguish the vapor and liquid density root. This is important for PC-SAFT (and any complicated) equation of state, as the phase density root must be solved iteratively, and a vapor density roots might converge to a liquid density root, or vs.

Furthermore, with the tangent point identified, the pressure density curve can be approximated extremely close to the real curve within density range $(0, \rho_{tg})$ by a two-parameter polynomial,

$$P = \rho kT + c_1 \rho^2 + c_2 \rho^3 \quad (2)$$

The two parameters, c_1 and c_2 , are functions of the tangent point only, thus the analytical derivatives would be easy to get. With the tangent point being identified, effort of solving the vapor and liquid phase density root for PC-SAFT would be reduced.

2.2. Squeezed functional pair

Even with the tangent point technique, dynamic simulation using PC-SAFT model still cannot meet the customer's performance requirement. Thus, we introduce another technique, the squeezed functional pair (which we call the super-linear approach) in solving VLE problems. Squeeze theorem states that if $f_L(x) \leq f(x) \leq f_U(x)$ for all x , then at some values of x (references) all three functions are equal. Such theorem can be extended into functionals $g_L(X_L)$ and $g_U(X_U)$ which replace $f_L(x)$ and $f_U(x)$ where both X_L and X_U are functions of x . Within a neighborhood of a reference $(x \pm dx)$, the "squeeze"-relation still holds by those functionals, and the complicated $f(x)$ can be simplified by its first order Taylor expansion. The gap of the functional pair would then be monitored to trigger necessary recalculation of $f(x)$ if value of x is moving away from the reference neighborhood.

3. Results

In this paper, two test cases were demonstrated to show that the performance improvement can be significant without losing model accuracy. The first is a binary mixture of methane and n-butane from [1,2]. The second one is a series of VLE flashes extracted from the high-pressure polyethylene process dynamic simulation.

Figure 2 shows the quality of applying the squeezed functional pair compares to the PC-SAFT VLE calculation without approximation. Noticing that applying the tangent point improves a little bit of the performance in identify the vapor and liquid density root, but it is still considered as the accurate modeling without any approximation. The approximation was by the squeezed functional pair directly applied to the reference solution and the neighborhood of the reference.

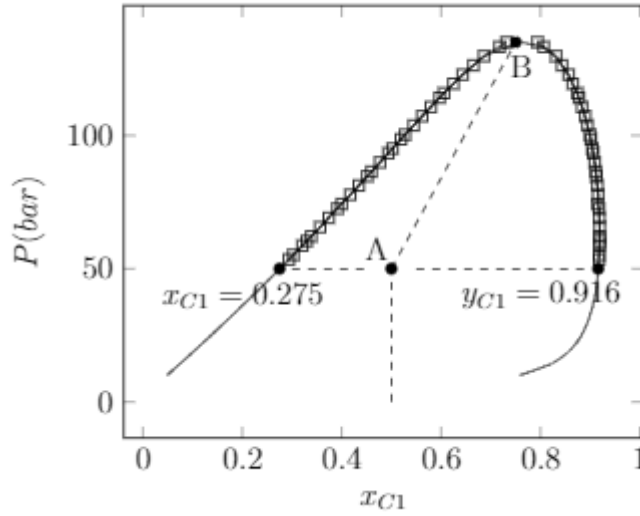


Fig 2. Methane and n-butane binary mixture VLE calculation was done at $T=21^{\circ}$. PC-SAFT model was applied to get the P-x-y diagram. If we calculate the VLE at equal-mole feed at $P=50$ bar, VLE solution was obtained with $y_{C1} = 0.916$ and $x_{C1} = 0.275$. If a series of VLE flash was done along section AB (feed and pressure changes), high quality of approximation (square markers) was obtained using the squeezed functional pair (super-linear).

Figure 3 shows the results from a series pressure-enthalpy specified VLE (totally 10,000 flashes). Results were represented by the temperature and vapor phase fraction values. High quality of approximation was obtained compares to the rigorous VLE calculation by PC-SAFT model, and the performance by the approximation was 3.8 seconds vs. the performance by the rigorous calculation as of 73 seconds. The model and component parameters for this mixture can be obtained from [2].

6. Conclusion

Phase density root identified by the tangent point approach helps high pressure VLE calculation without worrying about wrong phase density root. Significant performance improvement had been obtained by the squeezed functional approximation. With such improvement, dynamic simulation using modern and complicated thermodynamic models such as PC-SAFT is possible to meet or exceed customer's requirement. The new techniques introduced were generally applicable to all equation of state models.

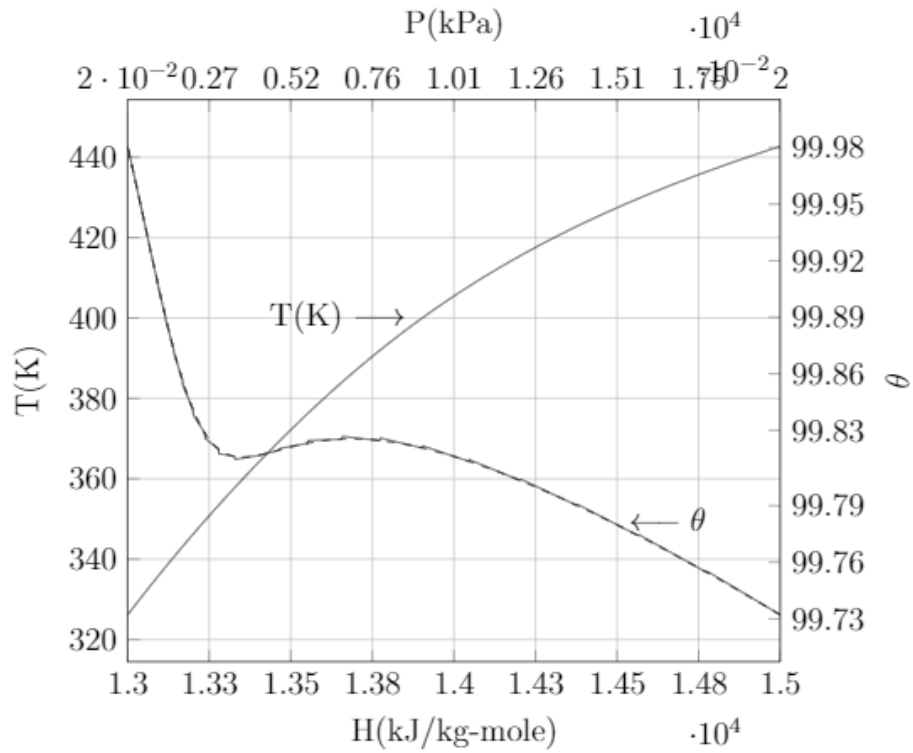


Fig 3. Dynamic simulation was done over 10,000 P-H specified VLE flashes with $P \in (200, 20000)$ kPa and $H \in (13000, 15000)$ kJ/kg-mol with results shown by temperature (T) and vapor phase fraction θ . Without squeezed functional pair approximation, it took about 73 seconds to finish. With approximation, we get extremely close solution with 3.8 second to finish all the VLE calculations on HP ZBook 15.

References

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- [2] Xu, G. Gerek Ince, N., J. Chem. Eng. Data. 65 (2020) 5643-5653.