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Parameterization of molecular-based equations of state

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Abstract

Despite significant advances in the development and formulation of molecular-based (MB) equations of state (EOS), their practical use has been limited, at least in part, by unavailability of the fluid-specific constants. In this work, we explore the possibility and consequences of obtaining the MBEOS parameters of a fluid directly from its critical constants T_c, P_c and acentric factor ω, as is done with cubic EOS.

Four different models are used as examples: perturbed hard chain theory in original (PHCT) and simplified (SPHCT) forms, Huang–Radosz version of the statistical associating fluid theory (SAFT), and the augmented van der Waals theory as implemented in the Boublík–Alder–Chen–Kreglewski (BACK) EOS. For each model, the scaled critical and saturation properties are computed and approximated by polynomial expansions. Using these, the molecular parameters can be related to the macroscopic properties T_c, P_c and ω. In this way it is *not* necessary to fit the EOS parameters to extensive experimental data, because the parameters obtained are fully equivalent to those generated from complex minimization techniques. In particular, the BACK EOS, parameterized in terms of T_c, P_c, ω and critical compressibility factor Z_c, gives excellent representation of the entire phase envelope. An alternative approach is also suggested where the experimental critical volume V_c and ω are matched, and a simple one-dimensional search is used to minimize the average absolute deviation of saturation pressures.

The techniques presented in this work provide a simple way to estimate MBEOS parameters for a wide variety of fluids, and can be readily extended to other MBEOS.

Keywords: PHCT; SPHCT; BACK; SAFT; Critical properties; Vapor–liquid equilibria

1. Introduction

It has been long recognized that molecular-based (MB) equations of state (EOS) present better predictive capabilities than their counterpart cubic EOS, due to their statistical mechanical basis. However, despite significant advances in the development and formulation of MBEOS, their practical use in industrial applications has been limited mainly for three reasons: (a) they are algebraically more complex than cubic EOS, which may discourage potential users, especially when they are left to work out by themselves the formulas for derived properties such as fugacities, enthalpies, etc.; (b) they are computationally more demanding as compared with the widely used cubic equations of state; and (c) fluid-specific constants are available for a limited number of compounds. With the increase in computer power by an order of 2 every 18 months, as well as the development of more efficient numerical methods, points (a) and (b) appear to be reaching a stable point. On the other hand, we believe that the unavailability of fluid-specific parameters is still a major obstacle in the application of MBEOS.

Traditionally, parameters for MBEOS are obtained by fitting experimental vapor pressure and liquid volumes. This technique presents as major drawbacks that (a) a fairly extensive body of experimental data on the pure substance is needed to obtain reasonable parameters; and (b) a sophisticated computer routine (e.g. a Marquardt or Nelder–Mead algorithm) is required to perform the multivariable search for the parameters that minimize the desired objective function. Both require more time and effort than the user of the MBEOS may be willing to expend.

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Several authors have studied the possibility and consequences of constraining a MBEOS to the experimental values of T_c and P_c. van Pelt et al. [1] fitted the parameters of the SPHCT EOS in this way, but did not take ω into account, using instead a Marquardt method to search for the parameter set that minimized the deviation of saturation pressures. Adding ω as a third constraint, Plačkov et al. [2] obtained parameters also for the SPHCT EOS using a nested iteration procedure which included Nelder–Mead minimization. Pfohl et al. [3] proposed an indirect method for determination of EOS parameters that enforce the correct reproduction of T_c and P_c, based on tracing the complete saturation line from a low temperature until the saturated phase volumes become equal. These authors showed that many EOS give best results when ω is constrained to the experimental value, but also that some models are unable to reproduce saturated pressures and liquid volumes simultaneously with reasonable precision. Gauter and Heidemann [4] proposed a parameterization of the Sanchez–Lacombe EOS in terms of T_c, P_c and ω as is done routinely with cubic equations of state. These authors had the advantage that the EOS has an exact solution at the critical point. In the present work, we propose a similarly simple method to obtain parameters for more complex MBEOS. The method is demonstrated by reference to a selected group of equations of state and fluids, but can be applied to any MBEOS and compound.

2. Relation between molecular and macroscopic parameters of MBEOS fluids

Molecular-based equations of state are normally formulated in terms of scaled temperature and density (or volume) variables:

$$Z = Z(\tilde{T}, \tilde{\rho}; \lambda_1, \lambda_2, \ldots), \qquad \tilde{T} \equiv \frac{T}{T^*}, \qquad \tilde{\rho} \equiv \frac{\rho}{\rho^*} \tag{1}$$

where T^* and ρ^* are scale factors related to characteristic molecular energy and size, and λ_1, λ_2, ... are parameters that define the physical model, e.g. molecular chain length, degree of polymerization, deviation from spherical shape, etc. The simplest definition of scaled pressure is

$$\tilde{P} = Z\tilde{T}\tilde{\rho} \tag{2}$$

This dimensionless formulation is equivalent to a molecular-based corresponding-states principle, in the sense that two fluids (to which the same MBEOS is applied) will have identical behavior in $\tilde{P} - \tilde{T} - \tilde{\rho}$ space if their molecular parameters λ_1, λ_2, ... are the same. All the models considered in this work contain only one such parameter; we denote this simply by λ and simplify Eq. (1) accordingly.

We start our study of each MBEOS by computing the generalized critical properties predicted by it. Solution of the classical critical stability criteria

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{\rho}}\right)_{\tilde{T}} = \left(\frac{\partial^2 \tilde{P}}{\partial \tilde{\rho}^2}\right)_{\tilde{T}} = 0 \tag{3}$$

yields scaled critical properties and critical compressibility factor as functions of λ:

$$\tilde{T}_c = \tilde{T}_c(\lambda), \qquad \tilde{\rho}_c = \tilde{\rho}_c(\lambda) \Rightarrow Z_c = Z_c(\lambda) \Rightarrow \tilde{P}_c = \tilde{P}_c(\lambda) \tag{4}$$

Because of the algebraic complexity of the MBEOS, numerical solution is almost invariably required (a notable exception is the Sanchez–Lacombe EOS studied by Gauter and Heidemann [4]). We use Newton–Raphson iteration in two variables with analytical derivatives for a set of λ values. It must be noted that the results are not affected by the particular temperature dependence that may be built into the scale factors T^* and ρ^*. The critical compressibility factor, in particular, is not rescalable and may limit the practical application of a given MBEOS.

Next, at subcritical temperatures $\tilde{T} < \tilde{T}_c$, we solve the phase equilibrium criteria

$$\ln \frac{\tilde{P}(\tilde{T}, \tilde{\rho}_g)}{\tilde{P}(\tilde{T}, \tilde{\rho}_f)} = \ln \frac{\phi(\tilde{T}, \tilde{\rho}_g)}{\phi(\tilde{T}, \tilde{\rho}_f)} = 0 \tag{5}$$

where ϕ is the fugacity coefficient, to obtain the scaled saturated phase densities and saturation pressure as functions of $\tilde{T}$ and λ:

$$\begin{aligned}\tilde{\rho}_f &= \tilde{\rho}_f(\tilde{T}; \lambda),\\ \tilde{\rho}_g &= \tilde{\rho}_g(\tilde{T}, \lambda) \Rightarrow \tilde{P}^{\text{sat}}\\ &= \tilde{P}(\tilde{T}, \tilde{\rho}_f \text{ or } \tilde{\rho}_g) = \tilde{P}^{\text{sat}}(\tilde{T}, \lambda)\end{aligned} \tag{6}$$

Here too, numerical solution proceeds by Newton–Raphson search with analytical derivatives. In the present work we have concentrated on developing correlations for the "omega temperature" $\tilde{T}_\omega$ that yields the acentric factor of the MBEOS fluid:

$$\begin{aligned}\tilde{T}_\omega &= 0.7\frac{T^*(T_c)}{T^*(0.7T_c)} \Rightarrow \omega\\ &= -1 - \log_{10}\left[\frac{\tilde{P}^{\text{sat}}(\tilde{T}_\omega; \lambda)}{\tilde{P}_c(\lambda)} \frac{T^*(0.7T_c)\rho^*(0.7T_c)}{T^*(T_c)\rho^*(T_c)}\right]\end{aligned} \tag{7}$$

Thus, in general, ω is a function of λ and of the molecular constants that express the temperature dependence of the scale factors. If these are constant, ω depends only on λ.

Finally, we map the MBEOS onto real fluid behavior. It is clear from the preceding equations that prescription of T^* and ρ^* (at each temperature, if not constant) and of λ permits conversion of the generalized scaled properties to non-scaled (no longer dimensionless) critical constants T_c, P_c, ρ_c and saturation values ρ_f, ρ_g, P^{sat}. The main point we wish to make in this paper is that *this process also works in the reverse direction*: having determined the scaled properties of the MBEOS fluid, specification of a small but sufficient number of macroscopic properties will fix the molecular constants. In essence, this procedure establishes the equivalence