Letter to the editor

Evaluation of an improved volume translation for the prediction of hydrocarbon volumetric properties

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Cubic equations of state are used in industry as well as at universities and it is well-known that their precision is limited. The poor description of the (saturated) liquid molar volumes of most pure compounds is one of the deficiencies very well known. Fig. 1 shows the description of pure *n*-hexane as an example. Many proposals exist, trying to improve this deficiency by superimposing volume translations according to the idea by Peneloux et al. [1].

de Sant' Ana et al. [2] compared some of these volume translations applicable to hydrocarbons. These authors evaluate the performance of temperature-independent volume translations as well as temperature-dependent volume translations. Their evaluation is based on a purely empirical method: they just compare the different calculation results with some experimental and pseudo-experimental data. The authors do not explicitly mention the major shortcoming of (most) temperature-dependent volume translations [3], although this shortcoming is most important for the PvT-range applicable to reservoir fluids they investigated (up to 120 MPa and 600 K) and although is not described well enough in literature, to guarantee that it will be recognized by all tempted to use such volume translations after reading the above article. In addition to pure theorists—who would never use such temperature-dependent volume translations therefore—anyone reading the above article ought to be informed about the danger connected with such temperature-dependent volume translations for any simple routine calculations.

Most of the temperature-dependent volume translations like those cited in the above manuscript or the one recently proposed by Ji and Lempe [4] shift the calculated isotherms by different values 'c' on the v-axis in a Pv-diagram—as if the deviation in volume was only a function of temperature. If the temperature dependence of such volume translation is adjusted in order to fine-tune the precision of calculated saturated liquid molar volumes, the critical isotherm is shifted much more than all other isotherms because the critical volume calculated with non-volume translated cubic EOS is very often the volume which is calculated least precisely (compare Fig. 1). Fig. 2 shows the same isotherms as
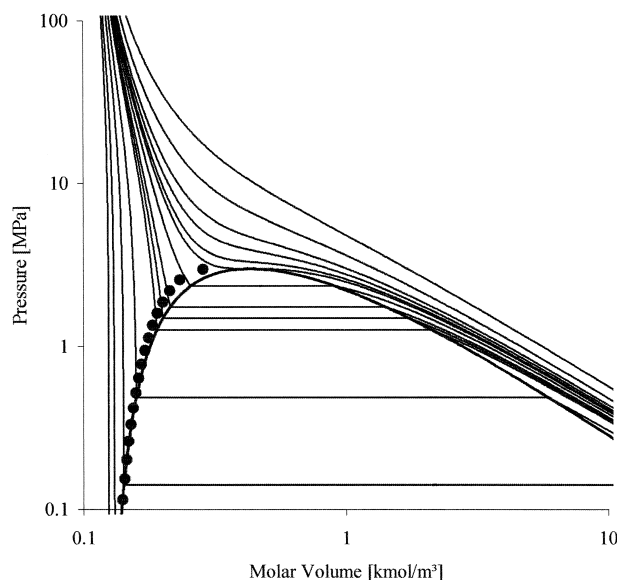
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Fig. 1. Pv-diagram for *n*-hexane. Lines = calculations with the Peng–Robinson EOS [6] (T_c = 506.43 K, P_c = 3.0123 MPa, ω = 0.264). ● = Experimental data [7].

Fig. 1 but the calculation results are volume translated according to the following equations by Magoulas and Tassios [5] which were also tested by de Sant' Ana et al. [2]

$$v^{\text{translated}} = v^{\text{original}} + c(T) \text{ with } c(T) = c_0 + (c_c - c_0)\exp(\beta|1 - T/T_c|)$$

Noticing the logarithmic scale in the figures, and looking at Fig. 1, it is evident, that the critical isotherm has to be shifted nearly as much as the co-volume of *n*-hexane. On the other hand, especially isotherms at low temperature are practically not shifted at all. Especially, at temperatures near the critical temperature, this leads to crossing isotherms in the region of high densities (compare Fig. 2). This 'high density' is not necessarily connected to (very) 'high pressure'—contrary to what is sometimes written in literature, because the critical pressure is quite low for some high-boiling compounds.

These crossing isotherms lead to an erroneous calculation of the reduction of liquid volume upon heating at isobaric condition or rising pressure in a closed vessel upon cooling. That is, most of these temperature-dependent volume translations sacrifice the self-consistent description of pure-component densities with a given EOS for a better description of saturated liquid volumes (or other parts of the PvT space). This neglects that the pure boiling liquid is only used for the determination pure-component properties in thermophysical property data laboratories and is by no means a measure for the volumetric problems engineers have to cope with all day if inconsistent temperature-dependent volume translations are used.

Because the deviations between calculated volumes and experimental data are not only a function of temperature but a function of temperature and volume, it is obvious, that volume translations that exclusively depend on temperature can only reproduce limited parts of the PvT-space well. Two of the volume translations tested by de Sant' Ana et al. had been adjusted to fluid properties along the
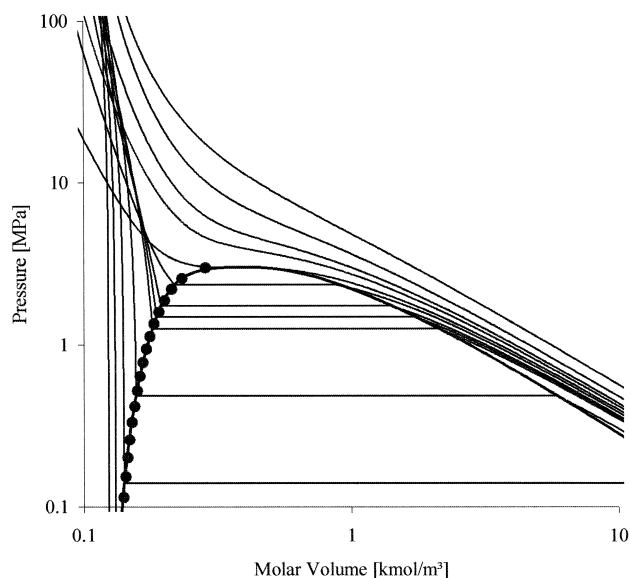
Fig. 2. Pv-diagram for *n*-hexane. Lines = calculations with the Peng–Robinson EOS [6] using the temperature-dependent volume translation [5] cited in this paper ($c_0 = 0.00061291$ kmol/m^3, $c_c = 0.0708305$ kmol/m^3, $\beta = -18.184726$). ● = Experimental data [7].

saturation curve while their own volume translation had been adjusted to the high-density/high-pressure PvT-space. Therefore, the results obtained by de Sant' Ana et al. show that the former translations are inferior to the ladder in the high pressure region (compare Fig. 2) while they are clearly superior in the vicinity of the critical point.

The use of temperature-dependent volume translations should be avoided outside the PvT-space where their constants have been fitted due to the empirical nature of these translations. Especially using the former (with a strong temperature dependence) unphysical results are likely to appear in the parts of the PvT-space of interest. Using one-fluid mixing rules, this inconsistent pure-component behaviour will also influence the reliability of calculated mixture densities.

References

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