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1873-2023: let's celebrate the 150th anniversary of the publication of Van der Waals' thesis

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Despite the criticism that the Van der Waals theory behind them is too simple, despite the many attempts to replace them with more sophisticated models, despite their well-documented shortcomings, it is a fact that the cubic equations of state (CEoS) are still around, and in industry in particular. Derived from the seminal work of Van der Waals, CEoS appear indeed as reference models for people from industry working on the simulation and design of processes involving from non-associating to weakly-associating compounds. Since the 1950's, people working on CEoS have gained experience on this class of models and a number of pertinent improvements have been proposed all through the years to overcome or reduce their shortcomings.

1) Since a few years, the potential of cubic equations of state seems to be rediscovered through works which brilliantly demonstrate that their accuracy can be dramatically improved by:

a) modifying the alpha function.
b) introducing a volume translation (the impact of a T-dependent volume correction needs to be discussed).
c) selecting with cautious the volumetric function that appears at the denominator of the attractive term.

2) As a noticeable feature, CEoS models are nearly all parameterized in a similar way based on the application of critical constraints. As a result, pure-component CEoS have the capacity to provide accurate description of phase-equilibrium (vapor pressure, enthalpy of vaporization ...) and energetic properties as well (heat capacity, enthalpy ...) but, as main limitations, they fail in correlating liquid-density and isothermal-compressibility data. The question we wish to address is: do these conclusions remain valid if CEoS parameters are fit on vapor-pressure and liquid-density data (which is classically done with SAFT-type EoS) ?

3) Contrary to what one might think, not everything has been said about improving CEoS for correlating multi-component systems. In this respect, recent work highlights the unsuspected potential of new advanced mixing rules based on Wilson's gE model. When applied to mixtures, CEoS rank among the best performing models (qualitatively and quantitatively) when compared to other equations of state using the same basis of comparison, provided that this basis is representative of the diversity of thermodynamic behavior of mixtures in nature.

In this study, we present some arguments to convince the reader that further development of this family of models is necessary and that promising results are expected in return.

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Preferred type of contribution:

☐ **Poster**

☒ **Oral**

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