Using the Spinodal of Single- and Multi-Component Fluids in the Development and Evaluation of Modern Equations of State

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Fluids are usually found in thermodynamically stable states, e.g. water sitting in a bottle. But they may be provoked into metastable states, like in the party trick where a bottle of beer is supercooled and freezes instantaneously when perturbed. The spinodal represents the ultimate limit of metastability, beyond which no homogeneous fluid state may exist. We discuss here how to use information about the spinodal both in the development and in the evaluation of equations of state (EoS). For this purpose, we have developed a robust methodology [1] for obtaining the spinodal of multicomponent fluids described with even the most sophisticated multiparameter EoS available. This allows us to devise inequality constraints that can be employed in the fitting of EoS for single-component fluids to avoid the inclusion of unphysical pseudo-stable states between the vapor and liquid spinodals. We find that even cubic EoS are in violation of some of these constraints. Using a selection of EoS including cubic, extended corresponding states, SAFT, and multiparameter EoS, we perform computations with pure species as well as two- and many-component mixtures of hydrocarbons to demonstrate the wide applicability of the approach. We quantify inconsistencies in predicted spinodals from these EoS, finding standard deviations in spinodal temperature up to 27 K in the case of a multi-component hydrocarbon vapor. We also identify a large region of the metastable domain that is currently inaccessible to experiments, which could spur new experimental or computational developments in order to provide improved properties data in this region, and to identify the states that define the spinodal.

References:

[1] P. Aursand, M. Aa. Gjennestad, E.Aursand, M. Hammer, Ø. Wilhelmsen, "The spinodal of single- and multi-component fluids and its role in the development of modern equations of state", *Fluid Ph. Equilibria*, 436 (2017) 98-112.