Calculation of critical points from Helmholtz-energy-explicit mixture models☆

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ABSTRACT

The calculation of the critical points for a mixture of fluids is of practical interest as the calculated critical points can be used to more reliably and efficiently construct phase envelopes. The number of stable critical points found can also provide insight into whether the mixture has an open or closed phase envelope.

In this work we have developed a reliable method for determining all the critical points for a mixture that is modeled with Helmholtz-energy-explicit equations of state. This method extends the algorithms developed in the literature for simpler equations of state to these more complex mixture models. These Helmholtz-energy-explicit equations of state could be either multi-fluid models or transformations of simple cubic equations of state to Helmholtz-energy-explicit forms. This algorithm locks onto the first criticality contour (the spinodal) and traces it to high density, thereby locating all relevant critical points. The necessary analytic derivatives of the residual Helmholtz energy, numerically validated values of the derivatives for validation, sample code, and additional figures and information are provided in the supplemental material.

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1. Introduction

The study of the calculation of the critical points (and critical lines) of mixtures forms a small subset of the broader field of phase equilibria of pure fluids and mixtures. If to begin we restrict ourselves to pure fluids, several phase equilibria are possible - vapor-liquid equilibria, solid-vapor equilibria, solid-solid-vapor triple points, and the like. Mixtures, on the other hand, involve all the complexities of pure fluid phase equilibria, and add another dimension to the problem - the consideration of the mixture composition. The addition of the mixture composition introduces a number of more complex phase equilibria, including critical lines, critical end points, liquid-liquid equilibria, and equilibria with solid phases [1].

The primary goal of this paper is to bring together the work related to the calculation of critical points of mixtures of fluids, and that of the developments in recent years of the high-accuracy Helmholtz-energy-explicit mixture models. Much of the existing literature on the calculation of mixture critical points focuses on well-behaved equations of state (cubics, cubics + excess Gibbs energy, etc.), which simplified the analysis somewhat. In this case we extend the previous models to more complex mixture models, which introduces some numerical challenges, as will be shown below.

The critical line, formed of the critical points, forms an important part of the global phase diagram constituting the vapor pressure curves of the pure components, multi-phase equilibria curves, azeotropic curves, and so on. Global phase diagrams are briefly described in the following section.

1.1. Critical points and curves

The majority of the scientific literature on the calculation of critical points of multi-component mixtures dates back to the 1970s. In fact, the history starts much earlier, with the work of Gibbs in 1876, and his establishment of the critical point conditions

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for a binary mixture [2]:

$$\left(\frac{\partial^2 G_{\mathrm{m}}}{\partial x_1^2}\right)_{T,p} = 0 \quad \& \quad \left(\frac{\partial^3 G_{\mathrm{m}}}{\partial x_1^3}\right)_{T,p} = 0, \tag{1}$$

where G_{m} is the molar Gibbs energy, T is the temperature, p is the pressure, and x_1 is the mole fraction of the first component.

Since 1970, a sizable body of literature has built up related to the calculation of critical points and critical lines for mixtures with two or more components. As a result, the literature survey presented here is intended to give the reader a sense of the more important advances in this field.

Beegle et al. [3] provide a general description of the mathematics involved in assessing the stability of a pure fluid or a mixture at a given state through the use of Legendre transformations applied to the internal energy.

Hicks and Young [4] provide a discussion of the calculation of critical points. They also provide a large body of experimental critical point data collected from their work and curation of other critical point data in literature.

Reid and Beegle [5] subsequently expressed the critical conditions in terms of Legendre transforms, which allows for a straightforward application of the mixture model to calculate the critical point. In this formulation, two matrix determinants (arising from Legendre transforms) must be simultaneously equated with zero, and this is the method further described and implemented in the analysis below.

Gubbins and Twu [6] studied some mixtures based on the combination of model inter-molecular interactions, from which they calculate both phase equilibria and critical loci. They are able to demonstrate a wide range of phase equilibrium behaviors through the use of these simple models.

Heidemann and Khalil [7] applied the criticality conditions and gave practical applications of the calculation of critical points through the use of cubic equations of state. Their work remains one of the most-cited contributions in this field.

Michelsen et al. [8] provided a novel algorithm for calculating critical points, as well as a discussion of the shape of the saturation curves in the vicinity of the critical point. Furthermore, extensive discussions of stability of the critical points and tangent plane distance analyses are provided.

Sadus [9] provided a review of literature on critical point evaluation and a description of some more complex critical point behavior, as well as a discussion of critical point transitions.

Kolář [10] applied the Predictive Soave-Redlich-Kwong (PSRK) model to several mixtures and calculated critical values with a method similar to that of Heidemann and Khalil [7]. They provide critical loci for a range of mixtures of technical interest.

Michelsen's book [11] provides an overview of the state-of-the-art of calculation of critical points, though as usual, the analysis is focused on cubic equations of state.

In the work of Deiters and Kraska [12], methods are presented to express the derivatives along the critical line, which can then be used to trace the critical line in a computationally efficient manner.

1.2. Global phase diagrams

Some of the work described above (e.g., Heidemann and Khalil) emphasized the calculation of the lowest density critical point for a given mixture composition, but there could be additional critical points. Methods that can find all critical points are useful from the standpoint of constructing global phase diagrams.

van Konynenburg and Scott [13] and Scott and van Konynenburg [14] developed much of the fundamental literature on mixture phase type classification. This scheme of classification of mixtures from Type I to Type V describes the critical curves found in phase diagrams. Type I is the simplest case, a continuous critical line between the critical points of the pure fluids in a binary mixture. More complex mixture classifications have been discovered; see for instance the book of Deiters and Kraska [12], and additional works in the field of global phase diagrams [15,16].

Hicks and Young [17] propose an algorithm for finding the critical points that is similar to the algorithm presented here, both in form and description. Their analysis is focused on cubic equations of state, but here we extend their analysis to multi-fluid models.

Cismondi and Michelsen [18] consider global phase diagrams for mixtures. They investigate a wide range of phase behaviors, and develop an algorithm that can automatically generate the phase diagrams for mixtures from Type I to Type V.

The extension of phase diagrams into three, four, and multi-phase equilibria (including solid phases) has been carried out in the work of Patel [19,20]. This simulation work involved the calculation of critical points and critical lines, as well as complex multi-phase equilibria, through the use of the homotopy continuation method.

van Pelt [21] apply the Hicks and Young algorithm [17] to systems modeled through the use of the perturbed hard chain model.

Hoteit et al. [22] propose a new and more reliable algorithm for the calculation of critical points (from the Peng-Robinson equation of state) that is based on nested and bounded iterations of Brent's method. It is compared with the method of Stradi et al. [23] and found to be more than a thousand times faster while they claim similar ability to locate critical points.

1.3. Helmholtz-energy-explicit mixture models

Cubic equations were the most-common formulation used to model the thermodynamic properties of mixtures prior to the advent of multi-fluid Helmholtz-energy-explicit mixture models, and even now are still in wide use. The majority of the literature dealing with the calculation of critical points described above is thus centered around cubic equation of state models, though much of the analysis can be used for multi-fluid Helmholtz-energy-explicit models as well.

Over the last few decades, multi-fluid Helmholtz-energy-explicit mixture models have been developed, the best known example being the GERG-2004 [24] and GERG-2008 [25] equations of state. These models are based on a framework that had been previously developed in parallel efforts by researchers in Germany and the USA [26–28].

As there is already a large body of scientific literature on the use of these multi-fluid Helmholtz-energy-explicit mixture models, and the models themselves are quite complex, it is incumbent on those who would extend these models to continue to use the same or functionally similar nomenclature. As much as possible, we have endeavored to ensure consistency with the nomenclature used in the existing literature. Furthermore, it is beyond the scope of this work to provide a complete description of the decades of work that has been carried out in this field. We therefore direct the reader to the relevant literature where possible and provide here a high-level discussion of the multi-fluid Helmholtz-energy-explicit mixture models.

The specific Helmholtz energy a is a fundamental thermodynamic potential; other properties of interest can be obtained through derivatives of the Helmholtz energy. The Helmholtz energy a is expressed as the sum of the ideal-gas contribution a^0 and the residual contribution a^{r}. In practice the non-dimensionalized Helmholtz energy is used rather than the specific Helmholtz energy, given by