



The spinodal of single- and multi-component fluids and its role in the development of modern equations of state



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ABSTRACT

The spinodal represents the limit of thermodynamic stability of a homogeneous fluid. In this work, we present a robust methodology to obtain the spinodal of multicomponent fluids described even with the most sophisticated equations of state (EoS) available. We elaborate how information about the spinodal and its uncertainty can contribute both in the development of modern EoS and to estimate their uncertainty in the metastable regions. Inequality constraints are presented that can be exploited in the fitting of modern EoS of single-component fluids to avoid inadmissible pseudo-stable states between the vapor and liquid spinodals. We find that even cubic EoS violate some of these constraints.

With the use of a selection of EoS representative of modern applications, we compare vapor and liquid spinodal curves, superheat and supersaturation limits from classic nucleation theory (CNT), and available experimental data for the superheat limit. Computations are performed with pure species found in natural gas, binary mixtures, as well as a multi-component natural gas mixture in order to demonstrate the scalability of the approach. We demonstrate that there are large inconsistencies in predicted spinodals from a wide range of EoS such as cubic EoS, extended corresponding state EoS, SAFT and multiparameter EoS. The overall standard deviation in the prediction of the spinodal temperatures were 1.4 K and 2.7 K for single- and multi-component liquid-spinodals and 6.3 K and 26.9 K for single- and multi-component vapor spinodals.

The relationship between the measurable limit of superheat, or supersaturation, and the theoretical concept of the spinodal is discussed. While nucleation rates from CNT can deviate orders of magnitude from experiments, we find that the limit of superheat from experiments agree within 1.0 K and 2.4 K with predictions from CNT for single- and multi-component fluids respectively. We demonstrate that a large part of the metastable domain of the phase diagram is currently unavailable to experiments, in particular for metastable vapor. Novel techniques, experimental or with computational simulations, should be developed to characterize the thermodynamic properties in these regions, and to identify the thermodynamic states that define the spinodal.

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1. Introduction

Metastable fluids can be found everywhere and continue to attract attention [1]. Recent examples include the ongoing discussion on cavitation of water at large negative pressures [2–6], magma erupting from volcanoes [7] and violent vapor-explosions

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from liquids spills in contact with a substantially warmer substance [8–11]. It is challenging to measure the properties of highly metastable fluids. By their own labile nature, they transform into a more stable phase via nucleation, where the nucleation process is triggered by thermal fluctuations. These fluctuations occur naturally, even in perfectly homogeneous fluids at equilibrium [12].

Properties of metastable fluids are central in the description of many processes. An important example is nucleation, which is ubiquitous in a wide range of physical, chemical, and biological processes. In nucleation theory, the thermodynamic state of the

critical embryo is within the metastable region of the fluid [12]. Even for the simple case of condensation of the noble gas argon, predictions of nucleation rates from classical nucleation theory (CNT) deviate more than 20 orders of magnitude from experiments. In contrast, we will here show that CNT predicts accurately the “limit of superheat” for many hydrocarbons, which represents the experimentally available limit of metastability of liquids. Some of the deviation between several theories [13,14] and experimental data is likely because of inaccuracies in current equations of state (EoS) in the metastable regions [13].

In the development of modern multiparameter EoS, for example for water [15], the thermodynamic properties of metastable fluid phases such as subcooled liquid (metastable with respect to solid-liquid) and superheated liquid (metastable with respect to the vapor-liquid) are included in the fitting procedure. The extrema for metastability are defined by the spinodal. At the spinodal, the homogeneous fluid becomes intrinsically unstable and the activation barrier for nucleation disappears. The unstable fluid will then spontaneously decompose into the more stable phases. From a thermodynamic point of view, much is known about the state of the fluid at the spinodal. For instance, for single-component fluids, several thermodynamic properties such as the bulk modulus and the inverse isobaric heat capacity equal zero. Therefore, information about the spinodal is valuable, both in the development of modern EoS and to estimate their uncertainty in the metastable regions. Moreover, a thermodynamically consistent behavior of the EoS in the unstable domain of the homogeneous fluid is a prerequisite for combining them with mass based density functional theory for studying interfacial phenomena [16].

A major challenge in the study of metastable fluids is that there are limitations to how close to the spinodal one can get in experiments with real fluids. No matter how careful an experiment has been carried out, thermal fluctuations that occur naturally in the fluid will trigger homogeneous nucleation before the spinodal has been reached, even though the metastable domain extends significantly further. Highly metastable states that are experimentally unavailable for bulk fluids can still be encountered in small cavities, or within the critical cluster or cavity during nucleation, and are thus of practical relevance. The experimentally attainable limit where a superheated liquid spontaneously transforms into vapor is known as the *limit of superheat* [1]. The most popular experimental technique for measuring the limit of superheat is the droplet explosion method, a technique dating back to the early work of Wakeshima and Takata [17] and Moore [18]. The droplet explosion method remains the most popular technique to date [8,11], and represents one of the techniques that can bring the liquid closest to the spinodal [19]. We shall in this work discuss how close to the spinodal it is possible to get experimentally, and how to get even closer.

From a theoretical perspective, we shall elaborate how information about the spinodal and its uncertainty can contribute both in the development of modern EoS and to estimate their uncertainty in the metastable regions. With the use of a selection of EoS with varying degree of complexity, we predict the spinodal curves for pure species and mixtures. The predicted spinodals are compared to both the limit of superheated liquid and supersaturated vapor from CNT and available experimental data. The present paper extends previous work on the topic spanning the last three decades [9,20–24]. Whereas previous studies have focused on cubic EoS, where obtaining the spinodal curve is straightforward, we present a general and robust approach based on thermodynamic stability analysis. This allows us to calculate and compare spinodals from a number of EoS with very different functional forms and levels of complexity. Moreover, while previous works have focused mostly on pure species, we calculate spinodals for hydrocarbon

mixtures with up to five components. We show that the functional form of the EoS can have a significant influence on the predicted spinodal.

2. Theory

In this section, we present the theoretical foundation for the work. We start in Sec. 2.1 by describing the different types of EoS that will be used. In Sec. 2.2, we discuss how the spinodal can be characterized, before we in Sec. 2.3 explain how to estimate the experimental limit of stability for a homogeneous fluid with classical nucleation theory.

2.1. Equations of state

2.1.1. Cubic EoS (PR, SRK)

The simplest type of EoS that can still predict the spinodal are the cubic EoS. These can in general be represented as

$$P = \frac{RT}{v - b} - \frac{a\alpha(T)}{(v - bm_1)(v - bm_2)}. \quad (1)$$

Here, P is the pressure, T is the temperature, R the universal gas constant, v the molar volume, and a , α , and b are parameters of the EoS. The constants m_1 and m_2 characterize various two-parameter cubic EoS. For instance, for the van der Waals (VdW) EoS, $m_1 = m_2 = 0$, for the Soave–Redlich–Kwong (SRK) EoS [25], $m_1 = 1$ and $m_2 = 0$, and for the Peng–Robinson (PR) EoS [26], $m_1 = -1 + \sqrt{2}$ and $m_2 = -1 - \sqrt{2}$. All these EoS are two-parameter cubic EoS in the sense that they use the two parameters a and b . For fluids with several components, mixing rules are used to compute the parameters a and b , which then depend on the composition.

2.1.2. Extended corresponding state EoS (SPUNG)

An extension of the corresponding state (CSP) methodology was initiated by Leach, Rowlinson and Watson as elaborated in Ref. [27], by including so-called “shape factors” that take into account how the mixture in consideration differs from the reference fluid(s). For pure components, this extension has a basis in statistical mechanics. If cubic EoS are used to calculate the shape factors, one may combine the strength of cubic EoS observed in VLE calculations with improved prediction of bulk properties obtained from a very accurate reference EoS. This methodology has also been referred to as the SPUNG EoS, and has proven to be both computationally fast as well as accurate [28]. We refer to Chapter 4 in Ref. [29] for further details.

2.1.3. Statistical associating fluid theory (SAFT)

Statistical Associating Fluid Theory (SAFT) gives EoS that are founded on statistical mechanics [30]. The perhaps most commonly used formulation is PC-SAFT [31] that has, in general, substantially improved accuracy in comparison with cubic EoS. Since PC-SAFT is founded on statistical mechanics and accounts for sizes and shapes of molecules, it is also expected to be the EoS with the largest predictive ability of the EoS considered in this work, in particular for polar substances and associating substances.

2.1.4. Multiparameter equations of state (GERG-2008)

Multiparameter EoS are today the most accurate EoS for the regions where thermodynamic property data are available. The EoS are founded on a comprehensive analysis of experimental data and a diligent optimization procedure, with functional forms optimized for accuracy. They have been devised for single-component fluids [15,32–36] and mixtures [37]. For some of these EoS, the thermodynamic properties of metastable fluid phases such as

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