Crossing the Widom-line – Supercritical pseudo-boiling

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ABSTRACT

Recent publications in the open literature have shown that supercritical fluid states are not homogeneously distributed but, in fact, can be differentiated into two distinct regions with gas-like and liquid-like properties, respectively. These regions are divided by an extension of the coexistence line, commonly called Widom line. This paper shows that a supercritical analog to subcritical phase change, pseudoboiling, does exist when crossing this demarcation. The supercritical state transition does not occur in a phase equilibrium but takes place over a finite temperature interval. While subcritical vaporization requires energy to overcome intermolecular attraction, supercritical state transitions additionally require energy to increase the temperature. It could be shown that the attractive potential is the dominant energy sink up to a reduced pressure of 1.5 for argon, nitrogen, oxygen, and water. The effect reduces with growing pressure and becomes negligible for $p/p_{cr} > 3$. Furthermore, a new equation for this Widom- or pseudoboiling-line is given. It exhibits improved accuracy over previously published equations; performing a limit analysis of the Clapeyron equation allows to express its sole parameter purely in terms of thermodynamic variables. This parameter can then be evaluated from an equation of state or from fluid data - no nonphysical fitting is required.

1. Introduction

While Andrews [1] introduced the notion of a critical point to terminate the vapor pressure curve more than 100 years ago, today there is not a common terminology on states exceeding the critical temperature or pressure (Bellan [2], Younglove [3]). The common view is that upon exceeding the critical point, liquids and gases do no longer exist. Instead, a structureless, homogeneous, continuous supercritical fluid prevails throughout the state space. Furthermore, given the vanishing of latent heat of vaporization and surface tension, a phase transition no longer occurs.

Fundamentally new insight has been gained in the last two decades, facilitated by advances in experimental and numerical methods. Inelastic X-ray scattering could be used to study dispersion, i.e. the dependence of the speed of sound on the frequency, which is a phenomenon found in liquids but not in gases. Using this technique, Simeoni at al. [4] and Gorelli et al. [5] were able to attribute this property to supercritical fluids at reduced pressures ($p_r = p/p_{cr}$) exceeding 1000. They concluded that the supercritical domain is divided into two regions with distinct respective liquid-like and gas-like behavior – much like at subcritical conditions. The

dividing line is an extension to the coexistence line. Gorelli suggested to extrapolate the Plank-Riedel equation, Eq. (1), into the supercritical domain,

$$\ln \left(\frac{p}{p_{cr}} \right) = a + b \frac{T_{cr}}{T} + c \ln \left(\frac{T}{T_{cr}} \right) \tag{1}$$

where $a = 4.270$, $b = -4.271$, and $c = 1.141$ have been fit to neon, oxygen, and nitrogen fluid data.

From a different perspective, Sciortino et al. [6] used molecular dynamics computations to investigate properties of this line emanating from the critical point which was later dubbed 'Widom' line. Fig. 1 illustrates this new view of supercritical states structure. The work of both groups is summarized by MacMillan and Stanley [7], Simeoni et al. [4] declare a new chapter to be open, new theories to be required. All research was concerned with the understanding of thermodynamic states and the identification of the boundary between them.

So far, no quantitative discussion has been given on processes in which this boundary is crossed. A name, however, exists: 'pseudoboiling' has been used by Okamoto et al. [8] and Oschwald et al. [9] to describe a supercritical liquid-like to gas-like transition. The term has originally been introduced by Kafengauz and Federov [10,11], who described a phenomenon in cooling pipes which resembled subcritical boiling – but at supercritical pressures.

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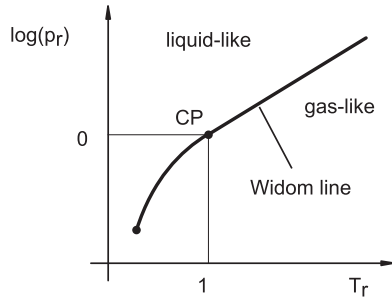E-mail address: daniel.banuti@dlr.de

Fig. 1. Fluid state plane and supercritical states structure with a liquid-like super-Widom fluid and a gas-like sub-Widom fluid. TP, triple point; CP, critical point; $T_r = T/T_{cr}$, $p_r = p/p_{cr}$.

Fig. 2. Construction of heat capacity based Widom line, for the example of nitrogen. (a) Nitrogen specific isobaric heat capacity $c_p(T)$ at sub- and supercritical pressures. (b) Positions of maximum c_p relative to coexistence line for nitrogen.

The concept is not undisputed: Hall [12] outright rejected it as "irrational and unnecessary because, clearly, two distinct phases do not exist at supercritical pressures", whereas Okamato et al. [8] called it a theoretical problem to be solved. Santoro and Gorelli [13] hypothesize there might be a "sluggish liquidlike-gaslike transformation mimicking the subcritical liquid-gas phase transition". Oschwald et al. [14,15] suggest that, unlike during subcritical vaporization, heat added to the fluid during pseudoboiling will act to both expand *and* heat it.

It is therefore the purpose of this paper to analyze processes which cross the Widom line from liquid-like to gas-like fluid states (and vice versa). The main question is: Can the concept of vaporization/condensation be applied to transitions between supercritical states?

2. Materials and methods

The approach taken here is mixed analytical and empirical. Thermodynamic relations and approximations are expressed in analytical form. All fluid data is taken from the NIST webbook [16]. First, the concept of pseudoboiling is evaluated using nitrogen data by Span et al. [17], with particular focus on the specific isobaric heat capacity of states at supercritical pressure. After this proof of concept, fluid data for argon (Tegeler et al. [18]) and oxygen (Schmidt and Wagner [19]) are investigated in a similar manner because of their expected similarity in behavior, following the corresponding states principle. Finally, water data (Wagner and Pruss [20]) are shown, explicitly to point out deviations for more complex fluids.

3. Results and discussion

3.1. Widom line equation

The original definition of the Widom line is the set of supercritical maximal thermodynamic correlation lengths [4]. However, this property is very hard to come by in a practical manner (May and Mausbach [21]). As a substitute, response functions – such as the heat capacity, the isothermal compressibility, and the thermal expansion – are used by several authors (e.g. Liu et al. [22], Xu et al. [23], Santoro and Gorelli [13], Ruppeiner et al. [24]). Regarding a state transition as a phenomenon of energy conversion in this paper, the specific isobaric heat capacity c_p is an appropriate marker. Fig. 2(a) illustrates this point using the example of nitrogen.

At the subcritical pressure 3 MPa, c_p diverges at the boiling temperature: here, heat is added during vaporization without an increase in temperature until all liquid is consumed. A distinct peak remains visible for supercritical pressures, flattening and moving to higher temperatures as the pressure increases from 4 MPa to 6 MPa.
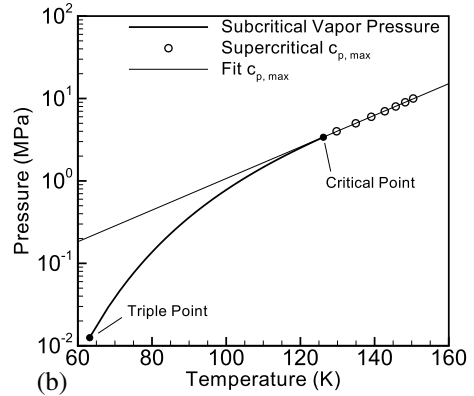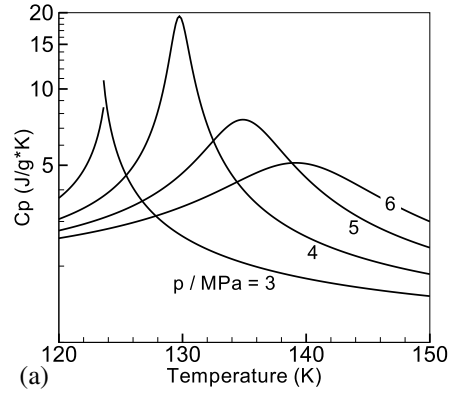
Fig. 2(b) shows how these peaks line up nicely when plotted into a $\log(p)/T$ diagram. Thus, an equation of the form

$$\frac{p_{pb}}{p_{cr}} = \exp\left[\frac{T_{cr}}{\theta_{pb}}\left(\frac{T_{pb}}{T_{cr}} - 1\right)\right] = \exp\left[A\left(\frac{T_{pb}}{T_{cr}} - 1\right)\right] \quad (2)$$

suitably describes the c_p based Widom line, where 'pb' and 'cr' denote properties along the pseudoboiling line and at the critical point, respectively. For dimensional reasons, the integration constant $1/\theta_{pb}$ can be interpreted as the inverse of a characteristic temperature. This parameter will now be determined from first principles.

Along the coexistence line from triple point to critical point, an equilibrium between the liquid (L) and the vapor (V) phase holds. This can be expressed mathematically by equating the respective phase differential Gibbs enthalpies which leads to the classical Clapeyron equation, Eq. (3),

$$\frac{dp}{dT} = \frac{s_V - s_L}{v_V - v_L} = \frac{1}{T}\frac{h_V - h_L}{v_V - v_L}. \quad (3)$$

The last equality holds as T remains constant during the transition from liquid to vapor. The latent heat of vaporization is $\Delta h = h_V - h_L$, the increase in specific volume and entropy are $\Delta v = v_V - v_L$ and $\Delta s = s_V - s_L$, respectively.

Classically, the Clapeyron equation is used up to the critical point. After all, the latent heat of vaporization vanishes, Eq. (3) loses its significance. However, not only does the jump in enthalpy (or entropy) vanish – the same is true for the specific volume. Thus, instead of invalidating the equation, progressing towards