



## The pseudocritical regions for supercritical water

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### HIGHLIGHTS

- Supercritical water behaves anomalously around the Widom lines.
- We calculated the location of the Widom lines for several thermodynamic functions.
- Simple quadratic fitting equations are given to describe these lines.

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### ABSTRACT

Vapour pressure curves and stability lines can be extended beyond the critical points into the supercritical domain by so-called Widom lines, along which some thermodynamic property undergoes a rapid change and liquid-like behaviour turns to vapour-like one. Knowledge about such lines is therefore important for thermohydraulic calculations and design. There are several properties that can be chosen as defining property of a Widom line. In this short note we calculate and compare several kinds of Widom lines for water.

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### 1. Introduction

Presently used Generation II and III reactors should be replaced in the next two-three decades with the so-called Generation IV reactors. The supercritical water cooled reactor (SCWR) is one of the proposed designs, working in pressures in the range of 25–30 MPa, above the critical pressure of the water (22.06 MPa). Due to the novelty of the working fluid, among other problems, new thermohydraulic challenges need to be solved (Ishiwatari et al., 2007; Mignot et al., 2007; Schulenberg and Starflinger, 2007; Baindur, 2008; Shan et al., 2009). The proper thermohydraulic design of Generation IV SCWRs is widely studied (Cheng and Yang, 2008; Ortega-Gómez et al., 2008; Fischer et al., 2009; Kiss et al., 2010) and for this design more fundamental analyses – mainly in the area of chemistry and physical chemistry – are needed (Imre et al., 2010, 2011; Svishchev and Guzonas, 2011). Some of our results might also be relevant in supercritical fossil fuel plants (already several hundreds of them working all around the world (Voss and Gould, 2001)), using the same coolant.

Two differences between pressurized liquid water (used in PWRs) and supercritical water (used in SCWRs) should be emphasized. The first is that, while in normal pressurized water one can cause phase transition (boiling) by increasing the temperature or by decreasing the pressure, this is not possible in supercritical water. We should mention here that for the planned SCWRs (Schulenberg and Starflinger, 2007), the working pressure is always supercritical, but the working temperature can fall below the critical value. In this sense, the water can be subcritical and consequently undergo a phase transition when the pressure is decreased. But it is still true that in supercritical water, the fluid will be always in single phase. Therefore difficult two-phase-flow related problems can be avoided. On the other hand, while in regular pressurized water most of the relevant properties (density, heat capacity, internal energy, etc.) change monotonously and slowly with temperature, this is not true in the supercritical region. Some of these quantities remain monotonous, but can exhibit very fast changes (like the sudden drop of the density in a narrow temperature range), while others cease to be monotonous and develop maxima (e.g., the heat capacity or compressibility) or minima (e.g., the speed of sound). Some of these problems – like the sudden drop of the miscibility of dissolved inorganic contaminants (Imre et al., 2011) – were already addressed. Still we think it advisable to map the “dangerous” temperature and pressure regions where these abrupt changes can happen, to help hydraulic designers to avoid these regions for already problematic parts, such as valves or narrow

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## Nomenclature

|       |   |
|-------|---|
| LOCA  | loss of coolant accident  |
| SCWR  | supercritical water cooled reactor                              |
| EoS   | equation of state   |
| PWR   | pressurized water reactor                                       |
| IAPWS | International Association for the Properties of Water and Steam |
| NIST  | National Institute of Standards and Technology                  |

necks. This is particularly important as some unusual thermohydraulic phenomena can occur in these regions, like the piston effect or deteriorated/improved heat transfer (Házi and Farkas, 2009; Mokry et al., 2010).

In Fig. 1, one can see the fluid phase diagram of water, i.e. solid phases are not shown. Up to the critical point ( $647 \pm 2$  K;  $22.064 \pm 0.001$  MPa (NIST)), above and below the vapour pressure line, one can find stable liquid water or steam, respectively. For the sake of clarity, metastable phases have been omitted (Debenedetti, 1996; Imre et al., 2002), although they can be important for the understanding of flashing and water hammer phenomena (Imre et al., 2010). The supercritical region is traditionally marked as a region in pressure–temperature space, bounded from the low temperature–low pressure side by two perpendicular lines (see the two dashed lines in Fig. 1) that are parallel to the two axes and unlimited toward high temperatures and high pressures. Recent results indicate that this definition of the supercritical region is not entirely precise (Artemenko et al., 2008; Simeoni et al., 2010). The difference of most thermodynamic properties between the fluid states marked by points A and B (640 K, 26 MPa and 650 K, 26 MPa, respectively) are much smaller than between the state marked by points B and C (650 K, 26 MPa and 660 K, 23 MPa, respectively), although B and C are in the supercritical region, whereas A is outside. The same is true for the B–C–D sequence, where D represents a state at 660 K and 22 MPa. The temperature, pressure and density data for the four points are given in Table 1, showing that the density hardly changes when the traditional “supercritical borders” are crossed (A to B or C to D), whereas it drops suddenly by a half for a move within the supercritical region (B to C). Evidently, the supercritical region should be divided into two regions, a liquid-like one and a vapour-like one. This difference can be explained by the fragmentation of the water molecule clusters existing in the liquid and liquid-like region (kept together by hydrogen-bonds) into smaller

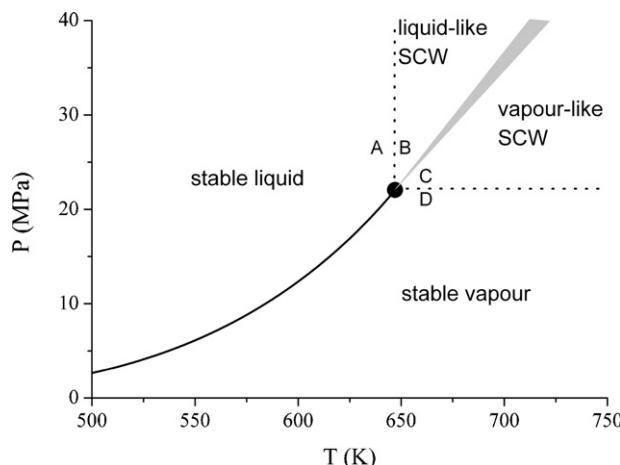


Fig. 1. Vapour pressure curve (solid line), critical point (black circle) and the supercritical region with the Widom zone of the water; stable phases are marked.

Table 1

Demonstration of the existence of a liquid-like and vapour-like region within the supercritical region.

|                   | T (K) | p (MPa) | $\rho$ (g/cm <sup>3</sup> ) |
|-------------------|-------|---------|-----------------------------|
| A (subcritical)   | 640   | 26      | 5.6600E–01                  |
| B (supercritical) | 650   | 26      | 5.0670E–01                  |
| C (supercritical) | 660   | 23      | 1.6371E–01                  |
| D (subcritical)   | 660   | 22      | 1.4194E–01                  |

groups or into individual molecules (Pártay et al., 2007), when they enter to the vapour-like region. The border between the two regions – which has been known for a while, but has not been properly defined before – can be defined in several ways. The first strict definition was given by Stanley and his co-workers. They defined this border (which – in  $(p,T)$  space – forms a line, starting from the critical point) as “...locus of specific heat maxima  $C_p^{\max}$  (“Widom line”) emanating from the critical point.” It can be also defined as the locus of the maxima of the correlation length (Xu et al., 2005). While formerly this border was sometimes mentioned as pseudo-critical or pseudo-spinodal, Stanley named it as the “Widom line” (not identical with the Fisher–Widom line), honouring the pioneering work of Widom on this field. We also would like to suggest using this name, because “pseudo-critical” and “pseudo-spinodal” are often used with different meanings.

For technical applications, the correlation length is not a handy quantity. This is in some sense also true for the isobaric heat capacity; in some non-isobaric processes it does not give the optimal definition for the Widom line. Therefore several alternative definitions were proposed. Generally, the Widom line (or rather Widom lines, see below) can be defined as the ridge of the extrema of a thermodynamic response function (e.g.  $C_p$ ,  $C_V$  or  $\kappa_T$ ) or any other quantity related to these functions (like the speed of sound). Alternatively, it can be defined as the locus of the inflection points (the maxima of the first-order derivative) of the density or the internal energy. These quantities are widely used in thermohydraulic calculations, and any of them would serve well as defining quantity. It should be mentioned here that these Widom lines (and hence most of the problems mentioned here) exist for most of the other real fluids too.

A closer investigation of Widom lines, however, shows that the extrema of the thermodynamic response functions do not exactly agree, and that therefore the outcome of the calculation of a Widom line depends on the choice of the defining thermodynamic function. Consequently, there is not a single Widom line, but a set of Widom lines for each fluid. Close to the critical point, the differences between these Widom lines are rather small, but can be much larger at higher pressures. Fortunately, far from the critical point, the above-mentioned extrema or inflections are less pronounced, and finally become negligibly small. But as near-critical conditions may occur in reactor design, it is worthwhile to map the Widom lines for technically important fluids like water in the relevant pressure–temperature range.

There are several other characteristic lines for real fluids partly or fully in the supercritical region. We should mention some of the Brown's curves (Brown, 1960; Deiters and de Reuck, 1997), which include the Joule inversion curve, the Joule–Thomson inversion curve, the Boyle curve and the isobar and isochors inflection curves, furthermore the Batschinski line (Brazhkin and Ryzhov, 2011) and the Frenkel line, which is a non-thermodynamic type boundary curve (Brazhkin et al., 2012a,b). Crossing these lines, we will not see any major changes in measurable properties relevant in thermohydraulic processes; furthermore some of them (for example the line describing a very shallow minimum of  $C_p$ ) are located at very high pressures, well outside the range of interest of this work.

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