

Widom Line Prediction by the Soave-Redlich-Kwong and Peng-Robinson Equations of State

A. Lamorgese*, W. Ambrosini, R. Mauri

*Department of Civil and Industrial Engineering,
Laboratory of Multiphase Reactive Flows,
Università di Pisa, I-56126 Pisa, Italy*

Abstract

For a pure component, we compute the characteristic isobaric inflection curve (a.k.a. the Widom line) for the Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) equations of state. Incidentally, we also show that using the Redlich-Kwong (RK) equation of state leads to a closed-form representation of the Widom line in the (T, v) plane. The SRK and the PR equations of state lead to almost coincident predictions for the Widom line; furthermore, comparing our numerical results with a correlation in reduced coordinates obtained by regression of experimental c_p data for CO₂ and water shows that the increased complexity of the SRK and PR equations (as compared to RK) allows improved agreement with the experimental data.

Keywords: Characteristic curves; Cubic equations of state; Thermodynamics.

1. Introduction

As is well known, the physical properties of a pure substance that enters its supercritical region by heating or cooling are strong functions of temperature and pressure, which can greatly affect heat transfer rates in practical applications. For example, in a supercritical constant pressure process, all physical properties of the substance show abrupt (but continuous) variations (as its behavior changes from liquid-like to vapor-like) within a narrow temperature range across the *pseudocritical* temperature, at which the isobaric heat capacity of the

*Email: andrea.lamorgese@unipi.it.

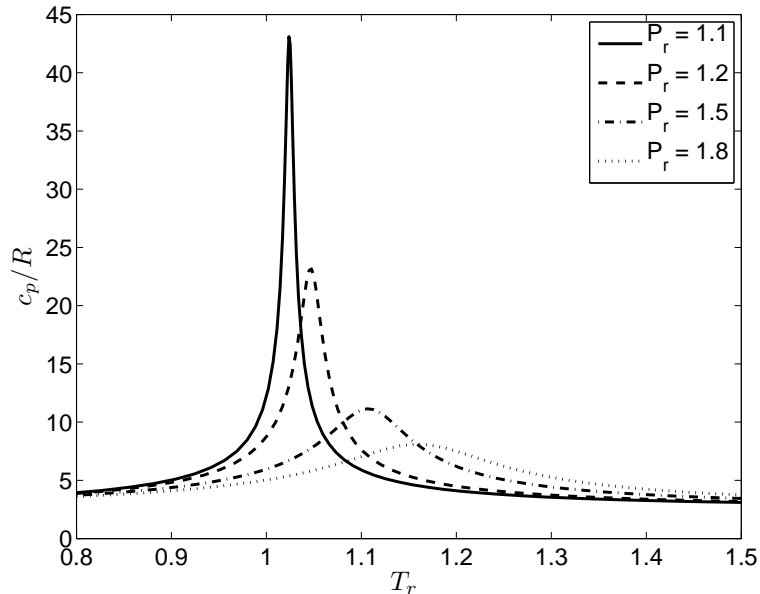


Figure 1: Isobaric heat capacity for a van der Waals fluid as a function of reduced temperature at different supercritical pressures ($P_r = P/P_c$ shown in the legend being the reduced pressure).

substance has a relative maximum, while its density, thermal conductivity, and dynamic viscosity decrease drastically. In particular, as the pressure increases further in the supercritical range, the relative maxima in the isobaric heat capacity decrease and move to higher temperatures. Collectively, the temperatures and pressures corresponding to the relative maxima in the c_p are called the pseudocritical (or Widom) line. However, at lower pressures (in particular at the critical pressure), abrupt (discontinuous) physical property variations characterize the substance in the neighborhood of its critical temperature, since any property which can be represented as a second-order derivative of a thermodynamic potential (such as, e.g., the isobaric heat capacity and the isothermal and isentropic compressibilities) will blow up at the critical point in a first-order transition.

Note that even the simplest (i.e., the van der Waals) EoS model that allows for a liquid-vapor transition can reproduce qualitative agreement with the aforementioned pseudocritical behavior of a pure substance. In fact, starting

from the van der Waals EoS in reduced coordinates,

$$\left(P_r + \frac{3}{v_r^2}\right) \left(v_r - \frac{1}{3}\right) = \frac{8}{3}T_r, \quad (1)$$

where $P_r \equiv P/P_c$, $T_r \equiv T/T_c$, $v_r \equiv v/v_c$ (where the c subscript denotes a critical value), and noting that the specific isochoric heat capacity for a classical van der Waals fluid is a constant, $c_v = 3R/2$ (with R denoting the universal gas constant), it is easily seen that the isobaric heat capacity takes the form (Johnston, 2014):

$$\frac{c_p}{R} - \frac{c_v}{R} = Z_c T_r \left(\frac{\partial v_r}{\partial T_r}\right)_{P_r} \left(\frac{\partial P_r}{\partial T_r}\right)_{v_r} = \frac{4T_r v_r^3}{4T_r v_r^3 - (3v_r - 1)^2}. \quad (2)$$

In Fig. 1, plots of this quantity as a function of (reduced) temperature at different supercritical pressures confirm that the relative maxima in the c_p move to higher temperatures as the pressure is increased further in the supercritical range. In fact, a straightforward calculation shows that these relative maxima are located for a van der Waals fluid at

$$P_r = 4T_r - 3, \quad (\text{and } T_r \geq 1) \quad (3)$$

in the (P_r, T_r) plane, or, equivalently, at $v_r = 1$ (and $T_r \geq 1$) in the (T_r, v_r) plane.

To date, although the Widom line has been studied in simple model systems, such as, e.g., a van der Waals or a Lennard-Jones fluid (Brazhkin and Ryzhov, 2011; May and Mausbach, 2012), a systematic discussion of the Widom line as predicted by the classical cubic EoS models, i.e., the van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson EoS has not been presented in the literature heretofore and is the principal result reported herein.

2. Parametric Construction of Characteristic Curves

Since our main objective in this paper is to discuss predictions of the Widom line based on different cubic EoS models, we first show that an assumption of Redlich-Kwong fluid properties leads to a closed form representation of the Widom line in the (T, v) plane. We begin by noting that the pseudocritical line can be defined thermodynamically by the condition:

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0, \quad (4)$$

where we have considered that $c_p = \left(\frac{\partial h}{\partial T}\right)_P$ in addition to $\left(\frac{\partial h}{\partial P}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_P$. Below, we will determine the Widom line by looking at the zero level set of $\left(\frac{\partial^2 T}{\partial v^2}\right)_P$. Before switching to reduced coordinates $P_r \equiv P/P_c$, $T_r \equiv T/T_c$, $v_r \equiv v/v_c$ (where the c subscript denotes a critical value), we note that the following two-parameter EoS (Schmidt and Wenzel, 1980)

$$P = \frac{RT}{v-b} - a \frac{\alpha(T_r)}{(v+\delta_1 b)(v+\delta_2 b)}, \quad (5)$$

with a and b denoting temperature-independent constants (while $\delta_{1,2}$ are parameters), comprises all four EoS models (i.e., van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson) discussed herein. Now, in reduced coordinates, Eq. (5) becomes

$$P_r = \frac{T_r}{x - \Omega_b} - \Omega_a \frac{\alpha(T_r)}{(x + \delta_1 \Omega_b)(x + \delta_2 \Omega_b)}, \quad (6)$$

where $x \equiv Z_c v_r$ (Z_c being the critical compressibility factor). With the SRK and PR EoS, Ω_a and Ω_b are defined based on the following relations (Smith et al., 2005):

$$a = \Omega_a \frac{(RT_c)^2}{P_c}, \quad \text{and} \quad b = \Omega_b \frac{RT_c}{P_c}. \quad (7)$$

Note that with the RK EoS the definition for Ω_a is with T_c raised to the 5/2 power (instead of T_c^2) in the first of these relations. For example, with the van der Waals EoS we have: $\delta_1 = \delta_2 = 0$, $Z_c = 3/8$, $\Omega_a = 27/64$, and $\Omega_b = 1/8$, and $\alpha(T_r) \equiv 1$. On the other hand, RK fluid properties are obtained by letting $\delta_1 = 0$, $\delta_2 = 1$, $Z_c = 1/3$, $\Omega_a = 1/[9(2^{1/3} - 1)]$, $\Omega_b = \frac{1}{3}(2^{1/3} - 1)$, and $\alpha(T_r) \equiv T_r^{-1/2}$. These last coefficients are still valid with the SRK EoS except that the α -function introduced by Soave (1972) incorporates a dependence on the Pitzer acentric factor, i.e.,

$$\alpha(T_r) = \left[1 + m(\omega)(1 - T_r^{1/2})\right]^2, \quad (8)$$

where $m(\omega) = 0.48 + 1.574\omega - 0.176\omega^2$. Finally, PR fluid properties are obtained by letting $\delta_1 = 1 + \sqrt{2}$, $\delta_2 = 1 - \sqrt{2}$, $Z_c = 0.3074013$, $\Omega_a = 0.45723552$, $\Omega_b = 0.077796074$. The α -function for the PR EoS is the same as that in Eq. (8), but with a slightly different prescription for $m(\omega)$, i.e.,

$$m(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2. \quad (9)$$

Before turning to the principal result discussed herein, which relates to the SRK and PR EoS models, we note that the pseudocritical line in the (T_r, x) plane corresponding to a choice of RK fluid properties can be written down in closed form after solving a quadratic equation, $0 = a_0(x) + a_1(x)T_r^{3/2} + a_2(x)T_r^3$, where

$$a_0(x) = \frac{\Omega_a^3}{4} \frac{10x^2 + 10\Omega_b x + 3\Omega_b^2}{x^5(x + \Omega_b)^5}, \quad (10)$$

$$a_1(x) = \frac{\Omega_a^2}{2} \frac{-5x^4 - 10\Omega_b x^3 + 5\Omega_b^2 x^2 + 4\Omega_b^3 x + 2\Omega_b^4}{x^4(x - \Omega_b)^3(x + \Omega_b)^4}, \quad (11)$$

$$a_2(x) = \frac{\Omega_a}{4} \frac{15x^4 - 30\Omega_b x^3 - 9\Omega_b^2 x^2 + 12\Omega_b^3 x + 8\Omega_b^4}{x^3(x - \Omega_b)^4(x + \Omega_b)^3}. \quad (12)$$

After some easy algebra, the result is:

$$T_r = \left\{ \Omega_a \frac{(x - \Omega_b)}{x(x + \Omega_b)(15x^4 - 30\Omega_b x^3 - 9\Omega_b^2 x^2 + 12\Omega_b^3 x + 8\Omega_b^4)} \times \right. \\ \left. [5x^4 + 10\Omega_b x^3 - 5\Omega_b^2 x^2 - 4\Omega_b^3 x - 2\Omega_b^4 + (5x^2 - \Omega_b x - 2\Omega_b^2) \times \right. \\ \left. \sqrt{-5x^4 + 20\Omega_b x^3 + 2\Omega_b^2 x^2 - 8\Omega_b^3 x - 5\Omega_b^4}] \right\}^{2/3}. \quad (13)$$

This locus is shown as the dot-dashed curve in Fig. 2. From this figure it also appears that predictions for the Widom line based on SRK and PR EoS are essentially identical for T_r values less than about 1.75; for larger values of T_r , however, the two curves are distinct. In addition, the RK prediction for the Widom line shows a significant departure from the Widom line ($v_r = 1$, $T_r \geq 1$) for the van der Waals EoS; finally, there is a significant discrepancy between the Widom lines for the SRK and PR EoS models as opposed to that for the RK EoS. Similar considerations apply to Fig. 3, showing Widom lines from the aforementioned EoS models in the (P_r, T_r) plane. Also shown is a correlation obtained by regression of experimental c_p data for CO₂ and water from Smith et al. (2013). In fact, based on their analysis of experimental data, these authors claim that the corresponding states principle can be used to estimate the pseudocritical line of a pure substance. We assume that this conclusion is accurate; however, there is still a noticeable difference in Fig. 3 between the Widom lines for the SRK and PR EoS models and that from the Smith et al. (2013) correlation. At least in part, such differences can be attributed to the temperature dependence in the α -function for the SRK (or PR) EoS (Soave, 1972; Peng and Robinson, 1976) being markedly different from that for the RK EoS. Since the

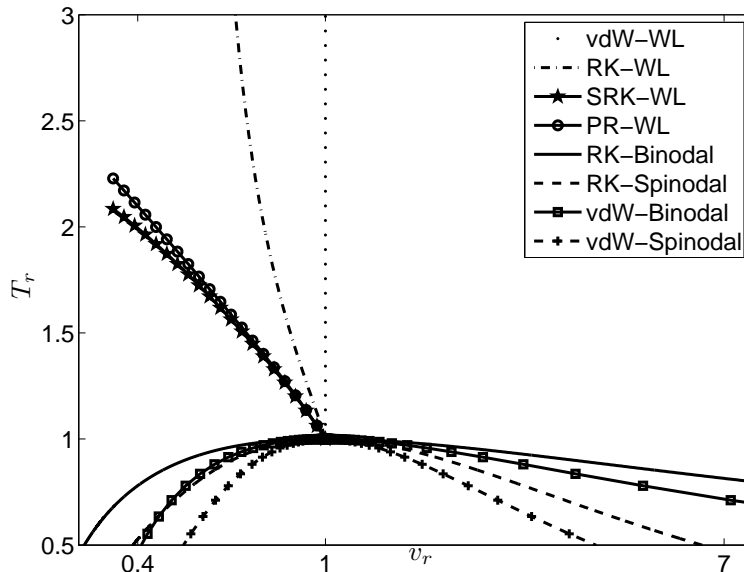


Figure 2: Widom lines in the (T_r, v_r) plane from the Peng-Robinson, Soave-Redlich-Kwong, Redlich-Kwong, and van der Waals EoS models. Also shown are the Redlich-Kwong and van der Waals binodal and spinodal curves.

Soave (1972) α -function passes the consistency test advocated by Le Guennec et al. (2016), it can be used at supercritical conditions (for values of the acentric factor in certain allowable ranges) up to a temperature $T_r^* = [1 + m^{-1}(\omega)]^2$, where it attains a relative minimum. However, as can be seen from Fig. 3, in our case (i.e., with both the SRK and PR EoS models) the α -function never attains its minimum in the supercritical range (for the values of the acentric factor $\omega = 0$ and $\omega = 0.34$ considered herein), so the oft-quoted issue with the Soave (1972) α -function that it might stop decreasing in the supercritical range as the reduced temperature increases (Mahmoodi and Sedigh, 2016; Gasem et al., 2001; Neau et al., 2009a,b) is not relevant here.

Acknowledgements

Financial support provided by MIUR (Grant no. PGR10DN9YV) is gratefully acknowledged.

References

Brazhkin, V., Ryzhov, V., 2011. Van der Waals supercritical fluid: Exact formulas for special lines. *J. Chem. Phys.* 135 (8), 084503.

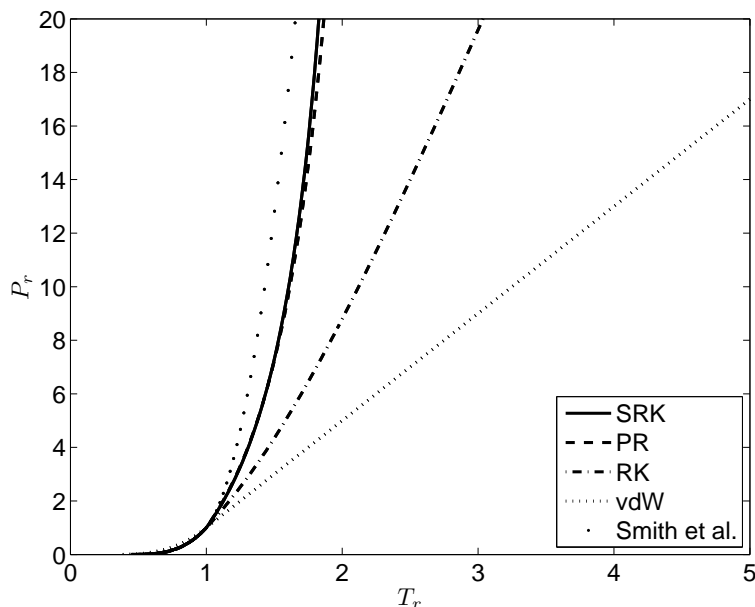


Figure 3: Widom lines in the (P_r, T_r) plane from the Peng-Robinson, Soave-Redlich-Kwong, Redlich-Kwong, and van der Waals EoS models. Also shown (dotted) is the correlation (obtained by regression of experimental c_p data for CO_2 and water) by Smith et al. (2013).

Gasem, K. A. M., Gao, W., Pan, Z., Robinson, R., 2001. A modified temperature dependence for the Peng–Robinson equation of state. *Fluid Phase Equilib.* 181 (1), 113–25.

Johnston, D. C., 2014. *Advances in Thermodynamics of the van der Waals Fluid*. Morgan & Claypool Publishers, San Rafael, CA (USA).

Le Guennec, Y., Lasala, S., Privat, R., Jaubert, J.-N., 2016. A consistency test for α -functions of cubic equations of state. *Fluid Phase Equilib.* 427, 513–38.

Mahmoodi, P., Sedigh, M., 2016. Soave alpha function at supercritical temperatures. *J. Supercrit. Fluids* 112, 22–36.

May, H.-O., Mausbach, P., 2012. Riemannian geometry study of vapor-liquid phase equilibria and supercritical behavior of the Lennard-Jones fluid. *Phys. Rev. E* 85 (3), 031201.

Neau, E., Hernández-Garduza, O., Escandell, J., Nicolas, C., Raspo, I., 2009a. The Soave, Twu and Boston–Mathias alpha functions in cubic equations of

- state: Part I. Theoretical analysis of their variations according to temperature. *Fluid Phase Equilib.* 276 (2), 87–93.
- Neau, E., Raspo, I., Escandell, J., Nicolas, C., Hernández-Garduza, O., 2009b. The Soave, Twu and Boston–Mathias alpha functions in cubic equations of state. Part II. Modeling of thermodynamic properties of pure compounds. *Fluid Phase Equilib.* 276 (2), 156–64.
- Peng, D.-Y., Robinson, D. B., 1976. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* 15 (1), 59–64.
- Schmidt, G., Wenzel, H., 1980. A modified van der Waals type equation of state. *Chem. Eng. Sci.* 35 (7), 1503–12.
- Smith, J. M., Van Ness, H. C., Abbott, M. M., 2005. *Introduction to Chemical Engineering Thermodynamics*, 7th Edition. McGraw-Hill, Boston.
- Smith, R., Inomata, H., Peters, C., 2013. *Introduction to Supercritical Fluids*. Elsevier, Amsterdam.
- Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* 27 (6), 1197–203.