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Similarity law for Widom lines and coexistence lines

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The coexistence line of a fluid separates liquid and gaseous states at subcritical pressures, ending at the critical point. Only recently, it became clear that the supercritical state space can likewise be divided into regions with liquidlike and gaslike properties, separated by an extension to the coexistence line. This crossover line is commonly referred to as the Widom line, and is characterized by large changes in density or enthalpy, manifesting as maxima in the thermodynamic response functions. Thus, a reliable representation of the coexistence line and the Widom line is important for sub- and supercritical applications that depend on an accurate prediction of fluid properties. While it is known for subcritical pressures that nondimensionalization with the respective species critical pressures p_{cr} and temperatures T_{cr} only collapses coexistence line data for simple fluids, this approach is used for Widom lines of all fluids. However, we show here that the Widom line does not adhere to the corresponding states principle, but instead to the extended corresponding states principle. We resolve this problem in two steps. First, we propose a Widom line functional based on the Clapeyron equation and derive an analytical, species specific expression for the only parameter from the Soave-Redlich-Kwong equation of state. This parameter is a function of the acentric factor ω and compares well with experimental data. Second, we introduce the scaled reduced pressure p_{r}^* to replace the previously used reduced pressure $p_{\mathrm{r}} = p/p_{\mathrm{cr}}$. We show that p_{r}^* is a function of the acentric factor only and can thus be readily determined from fluid property tables. It collapses both subcritical coexistence line and supercritical Widom line data over a wide range of species with acentric factors ranging from -0.38 (helium) to 0.34 (water), including alkanes up to n-hexane. By using p_{r}^*, the extended corresponding states principle can be applied within corresponding states principle formalism. Furthermore, p_{r}^* provides a theoretical foundation to compare Widom lines of different fluids.

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I. INTRODUCTION

The properties of near critical fluids are highly relevant for a wide range of important scientific topics, including carbon dioxide sequestration as a strategy to combat global warming [1] or submarine hydrothermal vents as a possible origin of life [2]. Supercritical fluids are applied as solvents in food and pharmaceutical processing [3,4] and as propellants [5,6]. Nonetheless, our understanding of these thermodynamic states is still limited: it has become clear that the notion of the supercritical state space as a featureless domain has to be revised. Experiments show that in extension to the subcritical coexistence line (CL), there exists a supercritical crossover line across which fluid properties change continuously from a liquidlike to a gaslike state over a small temperature interval [7–10]. It coincides conceptually with the so-called Widom line, originally introduced by Stanley and colleagues [11] as the locus of the maximum correlation length. As the correlation length is not readily available from macroscopic fluid data, the Widom line is often approximated as the set of states with extrema in the thermodynamic response functions [11–13], such as the isobaric specific heat capacity c_p [11,14–16], the isothermal compressibility κ_T [17,18], or the thermal expansion α_p [19]. This analogy is not undisputed. Brazhkin *et al.* [13] found that Widom line and specific heat maxima should exactly coincide with the isochore for Lennard-Jones fluids. May and Mausbach [20] criticized that there exists no formal way of determining the Widom line as the maximum of correlation length from response functions. Luo *et al.* [21] pointed out that response function maxima do not capture the original physical meaning of the Widom line. While the definitions based on different response functions are not equivalent, the loci of the maxima of isobaric specific heat capacity and coefficient of thermal expansion were found to practically coincide [13]. The line formed by maxima of c_p and α_p is understood here as the center of a crossover between liquid and gaseous states at both sub- and supercritical pressures. Figure 1 shows a schematic of this thermodynamic state space in terms of the reduced pressure $p_{\mathrm{r}} = p/p_{\mathrm{cr}}$ and reduced temperature $T_{\mathrm{r}} = T/T_{\mathrm{cr}}$.

Given the significance of the Widom line as a marker of strongly changing fluid properties, it is desirable to know its position in a state diagram without the need to determine response function maxima for every species. Nishikawa *et al.* [23] and Arias-Zugasti *et al.* [24] argued that the transition line should adhere to the corresponding states principle and be identical among different fluids when nondimensionalized with the respective fluid critical parameters. Other authors assumed this implicitly by comparing different fluid data in the same $p_{\mathrm{r}} - T_{\mathrm{r}}$ diagram [8,9,13,16]. Mathematical expressions for the Widom line have been proposed by Arias-Zugasti *et al.* [24] based on van der Waals' equation of state; by Gorelli *et al.* [8] using the Plank-Riedel vapor pressure equation for oxygen, nitrogen, and neon; and by Banuti [16] for nitrogen, oxygen, and argon.

None of the relations succeeds in accurately capturing the behavior of water or hydrogen, for which they were not specifically devised. Figure 2 shows that the equations of Gorelli *et al.* [8] and Banuti [16] are comparable for $p < 1.5 p_{\mathrm{cr}}$. Figure 2 compares the Widom line of oxygen, nitrogen, hydrogen, and water, obtained from the NIST database

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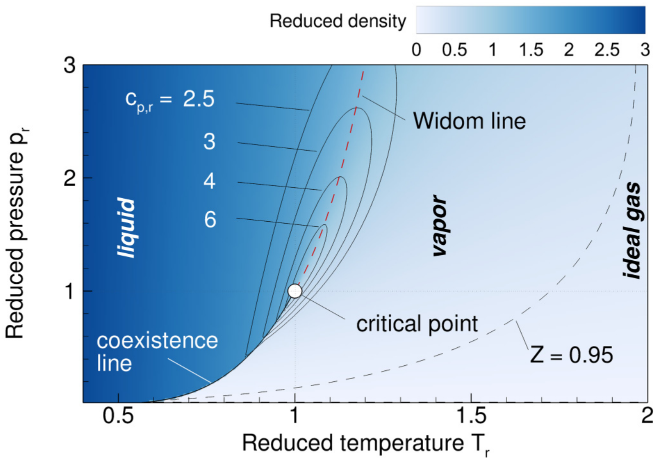


FIG. 1. Thermodynamic state plane and supercritical state structure. The Widom line is an extension to the coexistence line at supercritical pressure, defined as the locus of maximum isobaric heat capacity. It is a marker of the crossover between supercritical liquidlike and gaslike states. The contour represents the density distribution, showing the sharp transition at subcritical pressure and a smooth crossover at supercritical pressure. The dashed line at $Z = pv/(RT) = 0.95$ denotes the transition to an ideal gas. The reduced density ρ_r is ρ/ρ_{cr}, $c_{p,r} = c_p/c_{p,iG}$,$c_{p,iG} = \gamma R/(\gamma - 1)$, R is the gas constant, and γ the isentropic exponent. Data for oxygen is from NIST [22].

[22]. Only the simple fluids oxygen and nitrogen are found to collapse.

We have to conclude from this analysis that—contrary to the common assumption in the literature—the Widom line does not obey the corresponding states principle. This is a severe limitation, as we strictly cannot use data obtained from one species to interpret another.

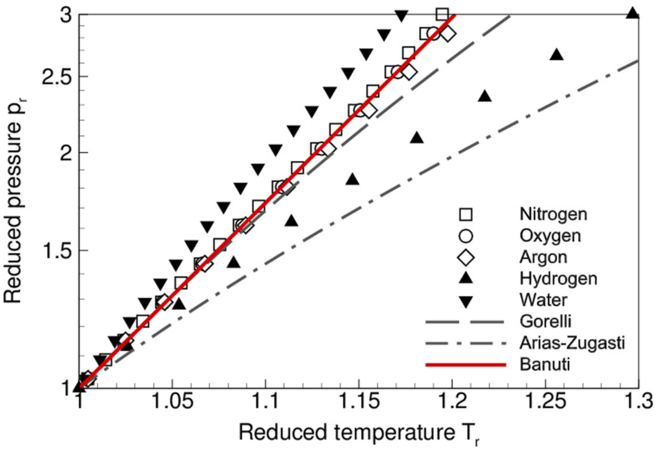


FIG. 2. Comparison of Widom line equations from Gorelli *et al.* [8], Arias-Zugasti *et al.* [24], and Banuti [16] with heat capacity peaks from NIST [22] for oxygen, nitrogen, water, and hydrogen. The relations of Gorelli *et al.* and Banuti are targeted towards capturing nitrogen and oxygen data (open symbols). None of the relations matches hydrogen or water (closed symbols) data; furthermore, data of different species do not collapse when plotted as functions of the reduced pressure and the reduced temperature.

In the present paper, we will resolve this issue in two steps. First, we show that like the coexistence line, the Widom line does obey the extended corresponding states principle. Specifically, we formulate the extended corresponding states principle with the acentric factor ω. We derive the relation between the slope of the Widom line and ω from first principles. Second, we introduce a nondimensional parameter, the *scaled reduced pressure* p_r^*. This quantity acts as a substitute for the reduced pressure $p_r = p/p_{cr}$ and collapses Widom lines and coexistence lines for a wide range of fluids. This similarity law now provides a simple way to compare results between different species.

II. THE CRITICAL SLOPE OF THE COEXISTENCE LINE

We start our similarity investigation with the notion that a macroscopic equilibrium state is characterized by an equality of Gibbs free energy $dg = vdp - sdT$, with specific volume v, pressure p, specific entropy s, and temperature T. Considering a vapor ($''$) and a liquid ($'$) phase in thermal and mechanical equilibrium, we can write

$$v'dp - s'dT = v''dp - s''dT. \tag{1}$$

For an isothermal transition, the specific enthalpy $h = s/T$, leading to the classical Clapeyron equation [25],

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v}, \tag{2}$$

which expresses the slope of the coexistence line dp/dT as a function of the difference Δ between the respective liquid and vapor states. Waring [26] suggested an exact rearrangement, using the compressibility factor $Z = pv/RT$ with the gas constant R,

$$\left[\frac{d(\ln p)}{d(1/T)}\right]_{\text{sat}} = -\frac{1}{R}\frac{\Delta h}{\Delta Z}, \tag{3}$$

which we will use to determine a suitable functional form for coexistence and Widom line similarity. Guggenheim [27] observed that the right-hand side of Eq. (3), $W = -\Delta h/(R\,\Delta Z)$, is approximately constant for the simple fluids Ar, Kr, Xe, N_2, O_2, CO, and CH_4. Integrating Eq. (3) with constant W, an integration constant $C = \ln p_{cr} - W/T_{cr}$ ensures that the critical point is part of the coexistence line. Finally, substituting $p = p_r p_{cr}$, $T = T_r T_{cr}$, and $A = W/T_{cr}$ yields

$$p_r = \exp\left[\frac{A}{T_r}(T_r - 1)\right], \tag{4}$$

valid for $T_r \leqslant 1$. For this equation, Zemansky [28] suggested $A = 5.3$ and Velasco and White [29] gave $A = 5.4$.

Thermodynamically, A can be interpreted as the nondimensional slope of the coexistence curve at the critical point. We introduce A_s as a species-dependent parameter that is no longer assumed universal. Then,

$$A_s = \frac{T_{cr}}{p_{cr}}\left(\frac{dp}{dT}\right)_{cr} = \left(\frac{d\ln p}{d\ln T}\right)_{cr}. \tag{5}$$

Using the thermodynamic relation given by Eq. (5), A_s can be determined from first principles. Consider the total derivative of pressure for a single component fluid,

$$dp = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv. \tag{6}$$

At the critical point $(\partial p/\partial v)_{T,\mathrm{cr}} = 0$, so that Eq. (6) can be recast in nondimensional form as

$$\frac{T_{\mathrm{cr}}}{p_{\mathrm{cr}}}\left(\frac{dp}{dT}\right)_{\mathrm{sat,cr}} = \left(\frac{\partial p_{\mathrm{r}}}{\partial T_{\mathrm{r}}}\right)_v = A_s. \tag{7}$$

It is worthwhile to discuss the implications of Eq. (7). In the coexistence region, $v = f(p,T)$ is no longer unique. Thus, an additional constraint needs to be introduced, such as Maxwell's criterion, to determine a point on the vapor pressure curve. The notable exception, as we now see, is the critical point. By definition, it terminates the vapor pressure curve towards high pressures and temperatures and is thus an element of it. However, Eq. (7) now allows one to calculate another property of the vapor pressure curve, i.e., its slope, without an additional constraint. Only fluid $p-v-T$ data in the form of an analytical equation of state is required to evaluate this. Furthermore, Eq. (7) is exact in an equilibrium context; no assumptions have been made, either mathematically or thermodynamically.

Having thus introduced an expression for the subcritical coexistence line, we can now analyze the supercritical case. At the critical point, the macroscopic phases become indistinguishable and an equality of the Gibbs energy is identically fulfilled, i.e., the difference fraction in Eq. (2) is transformed into a differential. Analogous to Guggenheim's observation that $d(\ln p)/dT$ in Eq. (3) be constant at subcritical pressure, we found that $d(\ln p)/dT$ remains constant for supercritical pressures up to $p_{\mathrm{r}} \lesssim 3$, leading to a form [16] similar to Eq. (4),

$$p_{\mathrm{r}} = \exp[A(T_{\mathrm{r}} - 1)] \quad \text{with } A \approx 5.5, \tag{8}$$

as a suitable expression of the Widom line for N_2, O_2, and Ar, holding for $T_{\mathrm{r}} \geqslant 1$. We can combine Eqs. (4) and (8) to obtain a generalized form, applicable to sub- and supercritical conditions,

$$p_{\mathrm{r}} = \exp\left[\frac{A_s}{\min(T_{\mathrm{r}},1)}(T_{\mathrm{r}} - 1)\right]. \tag{9}$$

We will now proceed to evaluate the sole parameter A_s by applying Eq. (7) to an equation of state. The Soave-Redlich-Kwong (SRK) equation [30] appears suitable, as its coefficients have been specifically determined to match vapor pressure curve data. It is defined as

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + bv}\Theta(T), \tag{10}$$

with

$$a = C_a\frac{(RT_{\mathrm{cr}})^2}{p_{\mathrm{cr}}}, \quad C_a = [9(2^{1/3} - 1)]^{-1}, \tag{11}$$

$$b = C_b\frac{RT_{\mathrm{cr}}}{p_{\mathrm{cr}}}, \quad C_b(2^{1/3} - 1)/3, \tag{12}$$

$$\Theta = [1 + \Omega(1 - \sqrt{T_{\mathrm{r}}})]^2, \tag{13}$$

$$\Omega = 0.480 + 1.574\omega - 0.176\omega^2. \tag{14}$$

TABLE I. Acentric factor ω and slope of the Widom line A_s for a number of species obtained from NIST [22]. Results are clustered (from top to bottom) as quantum gases, noble gases, diatomic molecules, hydrocarbons, and other complex molecules.

Species	ω	A_s
He	−0.382	3.516
H_2	−0.219	4.137
Ne	−0.0387	5.028
Ar	−0.00219	5.280
Kr	−0.0009	5.307
Xe	0.00363	5.326
O_2	0.0222	5.428
N_2	0.0372	5.589
F_2	0.0449	5.686
CO	0.050	5.750
CH_4	0.01142	5.386
C_2H_6	0.0993	5.687
C_3H_8	0.1524	5.882
C_4H_{10}	0.201	6.257
C_5H_{10}	0.251	6.117
C_6H_{12}	0.299	6.688
CO_2	0.22394	6.470
NH_3	0.25601	6.235
R124	0.28810	6.597
H_2O	0.3443	6.479

Using the compressibility factor at the critical point $Z_{\mathrm{cr}} = (p_{\mathrm{cr}}v_{\mathrm{cr}})/(RT_{\mathrm{cr}})$, Eq. (10) can be written in reduced, nondimensional form as

$$p_{\mathrm{r}} = \frac{T_{\mathrm{r}}}{Z_{\mathrm{cr}}v_{\mathrm{r}} - C_b} - \frac{C_a}{Z_{\mathrm{cr}}^2 v_{\mathrm{r}}^2 + Z_{\mathrm{cr}}v_{\mathrm{r}}}\Theta. \tag{15}$$

Applying Eq. (7) yields

$$A_{\mathrm{SRK}} = \frac{1}{Z_{\mathrm{cr}}v_{\mathrm{r}} - C_b} - \frac{C_a}{Z_{\mathrm{cr}}^2 v_{\mathrm{r}}^2 + Z_{\mathrm{cr}}v_{\mathrm{r}}}\frac{d\Theta}{dT_{\mathrm{r}}}, \tag{16}$$

with

$$\frac{d\Theta}{dT_{\mathrm{r}}} = -\frac{\Omega}{T_{\mathrm{r}}^{1/2}}[1 + \Omega(1 - \sqrt{T_{\mathrm{r}}})]. \tag{17}$$

At the critical point,

$$\left(\frac{d\Theta}{dT_{\mathrm{r}}}\right)_{\mathrm{cr}} = -\Omega. \tag{18}$$

Using $Z_{\mathrm{cr,SRK}} = 1/3$ [31], one obtains the numerical form,

$$A_{\mathrm{SRK}} = 5.51934 + 4.80640\omega - 0.537437\omega^2. \tag{19}$$

For validation of Eq. (19), we determine A_s for the locus of maximum specific isobaric heat capacity from the NIST database [22]; corresponding results are compiled in Table I and shown in Fig. 3. We see that agreement with the analytical model is good, especially for diatomic gases. With this, Eq. (9) can be used with variable coefficients A_s, from Eq. (19) or Table I, to match a wide range of fluids. Figure 4 shows a comparison with fluid data for oxygen, hydrogen, and water. It demonstrates that Eq. (8) with Table I is capable of describing the Widom lines for species with a wide range of acentric factors in good agreement up to a reduced pressure of

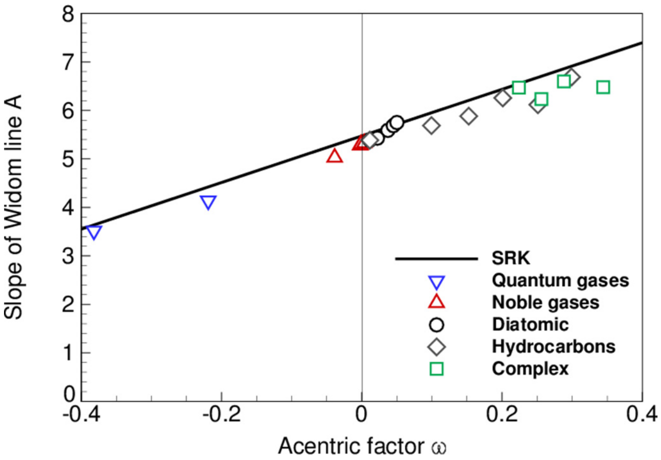


FIG. 3. Comparison of the slope of the Widom line A_s as a function of the acentric factor ω, obtained from the Soave-Redlich-Kwong equation of state (19) (line) and NIST reference data [22] (symbols).

$p_{\mathrm{r}} < 2$. Beyond, it constitutes a significant improvement over the formulation of Eq. (8) and other previously employed models [8,16,24].

III. AN EXTENDED SCALING LAW

We have shown that Eq. (8) with $A = 5.5$ is by no means general, but only applies to simple fluids in the context of the corresponding states principle. In contrast, Eq. (9) with the species specific coefficient A_s, obtained from Eq. (19) or Table I, is applicable to a wide range of species. Furthermore, the functional dependence of A_s on ω demonstrates that the crossover line adheres to the extended corresponding states principle. Indeed, Eq. (19) yields $A_s \approx 5.5 = A$ for $\omega = 0$.

What is missing is a nondimensional parameter akin to the reduced pressure of the corresponding states principle, which fulfills the extended corresponding states principle. This is obtained by rearranging Eq. (8) to

$$T_{\mathrm{r}} = \ln\left(p_{\mathrm{r}}^{1/A}\right) + 1, \tag{20}$$

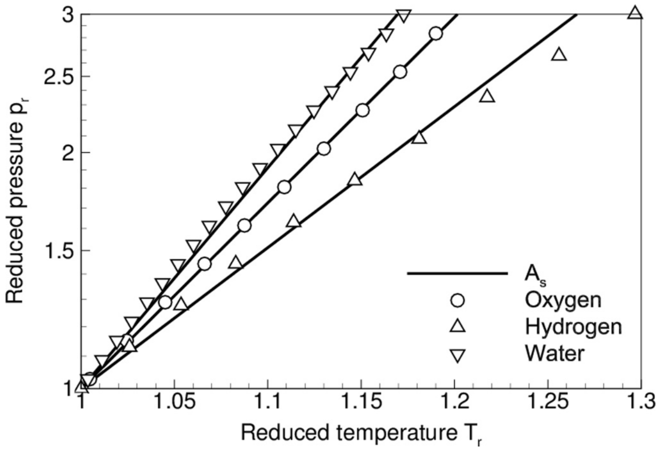
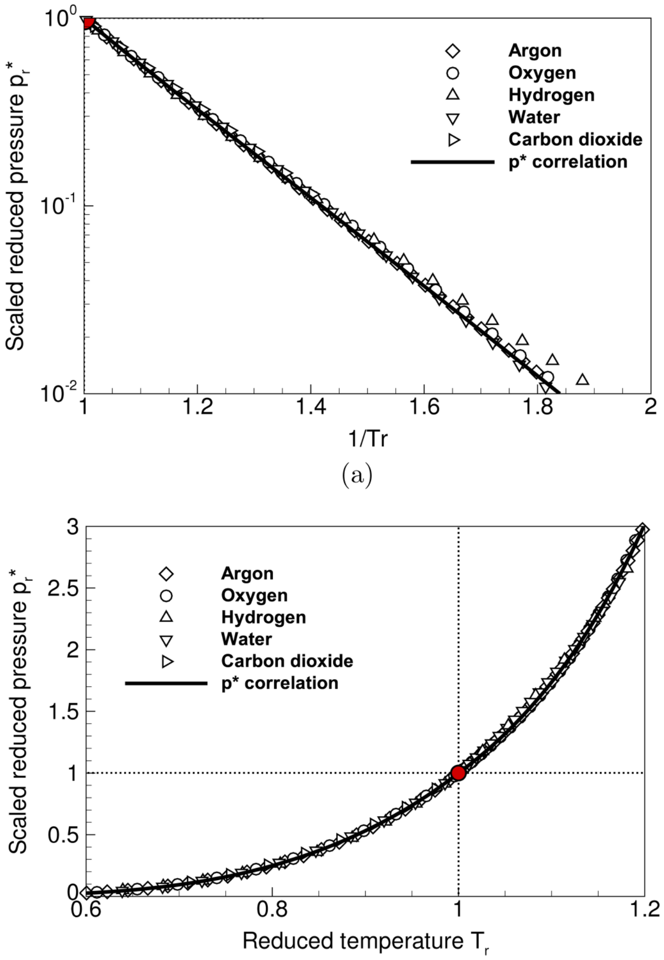


FIG. 4. Species specific Widom line from Eq. (9) and Table I for oxygen, hydrogen, and water.



(a)

(b)

FIG. 5. Collapse of (a) coexistence lines and (b) Widom lines from NIST data when using p_{r}^* of Eq. (21) instead of p_{r}. The p_{r}^* correlation is given by Eq. (22).

suggesting $p_{\mathrm{r}}^{1/A}$ as a suitable parameter. Ideally, we would like to reduce the scaled fluid behavior to that of a simple fluid; we thus use the nondimensional critical slope for vanishing acentric factor $A_0 = A(\omega = 0) = 5.52$ from Eq. (19) as a reference. We define the scaled reduced pressure p_{r}^* as a similarity parameter,

$$p_{\mathrm{r}}^* = p_{\mathrm{r}}^{(A_0/A_s)}. \tag{21}$$

Only the acentric factor is required to evaluate p_{r}^* using Eq. (19). Alternatively, A_s can be taken from Table I. We can show that p_{r}^* acts as a similarity parameter by raising both sides of Eq. (9) to the power of (A_0/A_s). This cancels the dependence on A_s in the exponent on the right-hand side and only species-independent coefficients remain. We have thus obtained a scaling law that fulfills the extended corresponding states principle.

Rewriting Eq. (9) using Eq. (21) should then yield a generalized equation for coexistence and Widom lines valid for all fluids within the extended corresponding states principle,

$$p_{\mathrm{r}}^* = \exp\left[\frac{A_0}{\min(T_{\mathrm{r}},1)}(T_{\mathrm{r}} - 1)\right]. \tag{22}$$

Figure 5 demonstrates the key findings of this paper: First, using the similarity parameter p_r^* instead of the classical reduced pressure p_r, the subcritical coexistence lines of a variety of fluids across a wide range of acentric factors are found to collapse. Such a mapping was not available previously for nonsimple fluids. Furthermore, the mapping here is straightforward to evaluate. Second, Fig. 5 illustrates the physical insight that the Widom line follows the extended corresponding states principle and can likewise be nondimensionalized using the scaled reduced pressure. This extends the current understanding by allowing comparison between nonsimple fluids. Finally, the approximate generalized equation for the coexistence and Widom lines, given by Eq. (22), matches NIST reference data satisfactorily for scaled reduced pressures up to three.

IV. CONCLUSIONS

This paper introduced the scaled reduced pressure p_r^* as an extended corresponding states generalization of the reduced pressure $p_r = p/p_{cr}$. The similarity parameter p_r^* allows for an excellent collapse of all evaluated coexistence and Widom lines for fluid data of 20 species with acentric factors ranging from −0.38 (helium) to 0.34 (water).

The Widom line and the coexistence line do not adhere to the corresponding states principle, and it was shown that nondimensionalization with critical pressure and temperature alone is insufficient to reduce data to a single state diagram. The scaled reduced pressure p_r^* remedies this and allows one to apply the extended corresponding states principle within corresponding states principle formalism. We showed that p_r^* is a function of the acentric factor ω alone and can thus be readily determined from known tabulated data.

For $0.5 < p_r < 3$, experimental fluid data of coexistence lines and Widom lines are well matched by Eq. (9), where the sole parameter A_s was shown to be equal to the nondimensional slope of the coexistence line at the critical point for a given species. For simple fluids ($\omega \approx 0$), the relation is valid to reduced pressures of three. We determined a species-dependent A_s in two ways: First, we calculated A_s exactly from a Soave-Redlich-Kwong equation of state. Second, we tabulated A_s for a number of species from experimental data. Agreement between theory and experiment is very good. This dependence on the acentric factor implies that the Widom line adheres to the extended corresponding states principle.

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