

On the universal behavior of some thermodynamic properties along the whole liquid-vapor coexistence curve

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When thermodynamic properties of a pure substance are transformed to reduced form by using both critical- and triple-point values, the corresponding experimental data along the whole liquid-vapor coexistence curve can be correlated with a very simple analytical expression that interpolates between the behavior near the triple and the critical points. The leading terms of this expression contain only two parameters: the critical exponent and the slope at the triple point. For a given thermodynamic property, the critical exponent has a universal character but the slope at the triple point can vary significantly from one substance to another. However, for certain thermodynamic properties including the difference of coexisting densities, the enthalpy of vaporization, and the surface tension of the saturated liquid, one finds that the slope at the triple point also has a nearly universal value for a wide class of fluids. These thermodynamic properties thus show a corresponding apparently universal behavior along the whole coexistence curve. © 2005 American Institute of Physics. [DOI: 10.1063/1.2035084]

I. INTRODUCTION

Many important practical applications require an accurate knowledge of thermodynamic properties along the whole liquid-vapor coexistence curve, from the triple point to the critical point.^{1,2} There are many empirical correlations for different thermodynamic properties that use the critical parameters and the acentric factor as input data. There are also proposals that include physical constants corresponding to each substance and a reduced number of adjustable coefficients. Obviously, the latter are more accurate but experimental data are required to evaluate the adjustable parameters, with the concomitant relative lack of predictability. In any case, it is very important to choose the appropriate model for a given class of fluids or even for a particular fluid at a particular temperature.

Corresponding-states correlations work particularly well at near-critical temperatures. However, more than 20 years ago, in order to correlate experimental data for the enthalpy of vaporization along the whole coexistence curve between the triple point (T_t) and the critical point (T_c), Torquato and Stell³ and Torquato and Smith⁴ used a dimensionless temperature,

$$\tau = \frac{T_c - T}{T_c - T_t}, \quad (1)$$

instead of the usual reduced temperature $T_r = T/T_c$. Then, they showed that the experimental data obtained by dividing the enthalpy of vaporization ΔH by its value at the triple point ΔH_t for six different fluids (propane, freon-12, nitrogen, argon, carbon dioxide, and water) exhibit an apparently universal behavior. A good fit for this behavior is given by the sum of six terms, each of them with one adjustable parameter and one fixed exponent.

Very recently, Meyra *et al.*⁵ have also analyzed the universal behavior of the enthalpy of vaporization but using the dimensionless temperature

$$t = \frac{T - T_t}{T_c - T_t} = 1 - \tau. \quad (2)$$

They find that the function

$$\Delta h(t) \equiv \frac{\Delta H}{\Delta H_t} = (1 - t)^{Z_c + Z_c^2 t} \quad (3)$$

fits the experimental data of Δh for five fluids (nitrogen, argon, methane, propylene, and water) very well. In Eq. (3), $Z_c = 0.292$ is the critical compressibility factor suggested by Guggenheim,⁶ so that this equation has no adjustable parameters.

Therefore, when the data of both the triple and critical points are taken as reference, the enthalpy of vaporization for

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a wide class of fluids seems to present a universal behavior that can be accurately described by a very simple empirical equation. This suggests that other thermodynamic properties might also behave similarly along the whole coexistence curve. The aim of the present work is to analyze this behavior, trying to understand it from a thermodynamic viewpoint. In particular, we propose a new expression for the temperature dependence of any thermodynamic property, along the whole liquid-vapor coexistence curve, that can help to understand why some of them, including the difference of coexisting densities (DCD), the enthalpy of vaporization (EV), and the surface tension of the saturated liquid (STSL), exhibit a universal behavior that can be described by a very simple two-parameter equation.

II. THEORETICAL CONSIDERATIONS

We consider a thermodynamic property $\psi(T)$ that has been made dimensionless in terms of the critical values of temperature T_c , pressure P_c , and density ρ_c . We are interested in the behavior of $\psi(T)$ only along the whole coexistence curve. Renormalization group theory predicts that asymptotically near the critical point $\psi(T)$ obeys the scaling law⁷

$$\psi(T) - \psi_c = A_\lambda \left(1 - \frac{T}{T_c}\right)^\lambda, \quad (4)$$

where $\psi_c = \psi(T_c)$, A_λ is the critical amplitude, and λ is the critical exponent along the coexistence curve. The critical exponents λ are universal while the amplitudes A_λ are system dependent although they satisfy a number of universal amplitude ratios.^{8,9} Furthermore, strictly speaking, the power law in (4) is the leading term of an extended scaling expression,¹⁰⁻¹² so that when it is used to correlate experimental data the exponent λ must be considered as an *effective* or *apparent* critical-point exponent.¹³

Unlike the critical point, the triple point of most fluids is easily accessible. Experiments near this point do not present any major difficulties, and the thermodynamic properties exhibit smooth behavior with respect to the temperature. Some simplifying approximations, such as that the vapor behaves as an ideal gas, are useful in the vicinity of the triple point, and in general one finds empirically that asymptotically near this point the temperature dependence of a given thermodynamic property $\psi(T)$ is given by the linear form

$$\psi(T) = \psi_t - B \frac{T - T_t}{T_c}, \quad (5)$$

where $\psi_t = \psi(T_t)$ and B is the slope of $\psi(T)$ at the triple point which can differ significantly from one substance to another.

Using the dimensionless temperature t , defined by Eq. (2), and the reduced thermodynamic property

$$\bar{\psi} \equiv \frac{\psi - \psi_c}{\psi_t - \psi_c}, \quad (6)$$

one can rewrite the power law in (4) as

$$\bar{\psi}(t) = A'_\lambda (1 - t)^\lambda, \quad (7)$$

where

$$A'_\lambda = \frac{A_\lambda}{\psi_t - \psi_c} \left(1 - \frac{T_t}{T_c}\right)^\lambda, \quad (8)$$

while the linear form in (5) becomes

$$\bar{\psi}(t) = 1 - bt, \quad (9)$$

where b is related to the slope of the function at the triple point:

$$b = \frac{B}{\psi_t - \psi_c} \left(1 - \frac{T_t}{T_c}\right). \quad (10)$$

In the present work we propose a function $\bar{\psi}(t)$ that goes from the value 1 at the triple point ($t=0$) to the value 0 at the critical point ($t=1$) reproducing the linear law in (9) near $t=0$ and the power law in (7) near $t=1$. In particular, we factorize $\bar{\psi}(t)$ into two contributions, one accounting for the power law in (7) and the other being analytical at the critical point. We assume the Darboux form of singularity:¹⁴

$$\bar{\psi}(t) = A'_\lambda (1 - t)^\lambda f(t), \quad (11)$$

where $f(t)$ is a bounded regular function along the whole coexistence curve verifying the *boundary* conditions

$$f(1) = 1, \quad (12)$$

and

$$f(0) = 1/A'_\lambda. \quad (13)$$

Dividing both sides of Eq. (11) by $(1 - t)^\lambda$, and taking natural logarithms, one obtains

$$\ln \left[\frac{\bar{\psi}(t)}{(1 - t)^\lambda} \right] = \ln A'_\lambda + \ln f(t) \equiv g(t), \quad (14)$$

where, from (12) and (13), one has

$$g(1) = \ln A'_\lambda, \quad (15)$$

and

$$g(0) = 0. \quad (16)$$

Therefore, the function $g(t)$ defined by Eq. (14) is also a bounded regular function in the range $0 \leq t \leq 1$. Expanding $g(t)$ in a Taylor series about $t=0$, and using Eq. (16), one obtains

$$g(t) = \sum_{n=1}^{\infty} a_n t^n, \quad (17)$$

where

$$a_n = \frac{1}{n!} \left(\frac{d^n g(t)}{dt^n} \right)_{t=0}. \quad (18)$$

Furthermore, from Eqs. (15) and (17)

$$\sum_{n=1}^{\infty} a_n = \ln A'_\lambda. \quad (19)$$

Hence, substitution of Eq. (17) into Eq. (14) yields

TABLE I. Typical values for the relevant parameters of the problem for the substances studied. The reduced STSL is given in units of $k_B^{1/3}$, k_B being the Boltzmann constant.

ψ	ψ_c	ψ_t	λ	A_λ	A'_λ	b	$ r_1 $
$\frac{\Delta\rho}{\rho_c}$	0	(2.5, 3.4)	$\sim 0.35^a$	(3.5, 4.0) ^b	~ 1	(0.29, 0.41)	(0.0, 0.06)
$\frac{\sigma}{P_c^{2/3}T_c^{1/3}}$	0	(0.14, 0.43)	$\sim 1.23^c$	(0.45, 0.70) ^d	~ 1	(1.18, 1.28)	(0.0, 0.05)
$\frac{\Delta H}{RT_c}$	0	(5.2, 9.0)	$\sim 0.38^e$	(5.0, 7.7) ^f	~ 1	(0.30, 0.54)	(0.0, 0.16)
$\frac{P}{P_c}$	1	~ 0	1	(-5.7, -7.4) ^g	(2.0, 4.7)	(0.0, 0.28)	(0.03, 0.55)

^aReference 16.^bReference 13.^cReference 17.^dReference 18.^eReference 19.^fReference 20.^gReference 21.

$$\bar{\psi}(t) = \exp\left[\sum_{n=1}^{\infty} a_n t^n\right] (1-t)^\lambda. \quad (20)$$

We note that asymptotically near the critical point Eq. (20) becomes the power law in (7),

$$\bar{\psi}(t) = \exp\left[\sum_{n=1}^{\infty} a_n\right] (1-t)^\lambda = A'_\lambda (1-t)^\lambda \quad (1-t \ll 1), \quad (21)$$

while near the triple point Eq. (20) becomes the linear law in (9)

$$\bar{\psi}(t) = 1 - (\lambda - a_1)t = 1 - bt \quad (t \ll 1), \quad (22)$$

with $b = \lambda - a_1$. Equations (21) and (22) show that Eq. (20) can be regarded as an interpolation between the critical- and triple-point behaviors.

The practical application of Eq. (20) requires the series to be truncated at some finite order. From Eq. (19), one can define the remainder

$$r_k \equiv \sum_{n=k+1}^{\infty} a_n = \ln A'_\lambda - \sum_{n=1}^k a_n, \quad (23)$$

and, if $|r_k| \ll 1$, one can approximate Eq. (20) by the truncated form

$$\bar{\psi}(t) = \exp\left[\sum_{n=1}^k a_n t^n\right] (1-t)^\lambda. \quad (24)$$

For example, if $|r_1| = |\ln A'_\lambda - a_1| \ll 1$ one can truncate the series in Eq. (20) at first order in t and, taking into account that $a_1 = \lambda - b$, one obtains

$$\bar{\psi}(t) = e^{(\lambda-b)t} (1-t)^\lambda, \quad (25)$$

with only two parameters: the critical exponent λ and the slope at the triple point b . Equation (25) could provide an explanation of the apparent universality of some thermodynamic properties along the whole coexistence curve when they are converted to reduced form by using both critical- and triple-point data. This universality would be presented by the thermodynamic properties of fluids when both the

slope b varies very little and the condition of Eq. (25) is justified ($|r_1| \ll 1$).

III. RESULTS

In order to check Eq. (25), we analyzed the t dependence of four dimensionless thermodynamic properties [the DCD, $\Delta\rho/\rho_c$; the STSL, $\sigma/P_c^{2/3}(k_B T_c)^{1/3}$; the EV, $\Delta H/RT_c$; and the saturation pressure (SP), P/P_c] along the whole coexistence curve for a set of 13 pure substances (Ar, Kr, Xe, N₂, CO₂, C₂H₄, C₃H₆, C₃H₈, C₄H₁₀, C₆H₁₄, R22, R125, and R134a). We took 11 data (including the values at the triple point and at the critical point) for each thermodynamic property and for each substance from the NIST data bank.¹⁵ For these substances the reduced triple-point temperature T_t/T_c lies in the range [0.231(C₃H₈), 0.712(CO₂)]. Other typical values for the relevant parameters of the problem are given in Table I. While the apparent critical exponents λ can be considered as universal for each property, the triple-point values ψ_t and the critical amplitudes A_λ are system dependent. However, the reduced amplitude A'_λ is close to unity for the DCD, STSL, and EV, although it is system dependent for the SP. The slope at the triple point b has similar values for different substances for the DCD and STSL, but presents more dispersion for the EV and especially for the SP. The last column gives the value of the parameter $|r_1|$. One can see that the convergence condition $|r_1| \ll 1$ is well satisfied for all the substances considered for the DCD and STSL, is reasonably satisfied for the EV, but in general is not satisfied for the SP.

Therefore, for the substances considered, one can expect the DCD and STSL to present a universal behavior that can be represented by Eq. (25). For the EV, one can expect the data to be more dispersed but Eq. (25) to be in general applicable. No such universality is to be expected for the SP, however, although Eq. (25) might be used to correlate the experimental data for some substances (those for which $|r_1| \ll 1$). The confirmation of these predictions is shown in Figs. 1–3. These are plots of the experimental data for the four thermodynamic properties considered, reduced by means of Eq. (6), versus the reduced temperature t , Eq. (2), for the aforementioned substances. Figures 1(a) and 1(b) show that, for all the substances considered, the DCD and STSL data, respectively, reduce to a single curve that can be represented

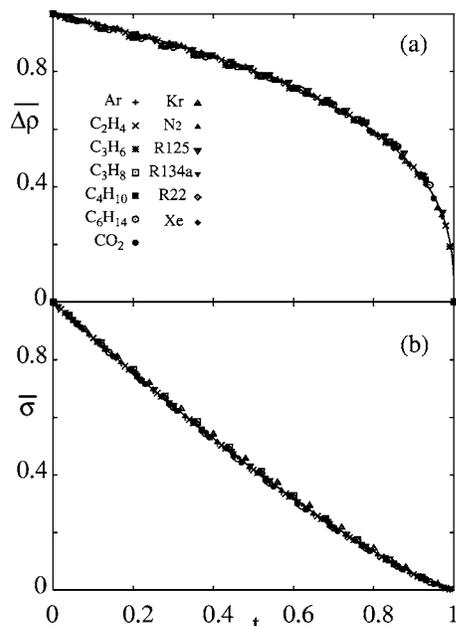


FIG. 1. Plot of the reduced DCD $\overline{\Delta\rho}$ (a) and STSL $\overline{\sigma}$ (b) [see Eq. (6)] vs the reduced temperature t . The symbols represent data for the fluids considered (Ref. 15) and the solid lines represent Eq. (25) with the values of parameters given in Table II.

by Eq. (25) (solid lines). The parameters λ and b for these curves are given in Table II. The critical exponent λ was taken as fixed, while the parameter b was least-squares fitted. The resulting values of b are within the ranges given in Table I. Figure 2 shows that the EV data also correspond to a single curve, although the dispersion is greater than in the former two cases. The values of the parameters λ and b for a fit to Eq. (25) with λ fixed are also given in Table II. Figure 3 shows that the SP data do not correspond to any universal curve. Nevertheless, the data of those substances satisfying the convergence condition $|r_1| \ll 1$ can also be represented by using Eq. (25). This is the case for CO_2 ($|r_1| \sim 0.03$) and for the family of noble gases ($|r_1| \sim 0.06$). In these cases, we took $\lambda=1$ and fitted b . The results were $b=0.271$ for CO_2 and $b=0.065$ for the noble gases. We found that the remaining SP data for each substance are well described by Eq. (24) with $k=2$, taking λ and b as input and the new parameter a_2 as adjustable.

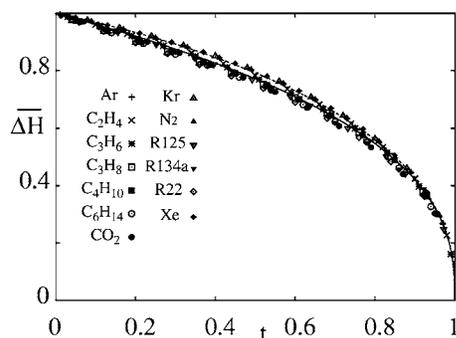


FIG. 2. Plot of the reduced EV $\overline{\Delta H}$ [see Eq. (6)] vs the reduced temperature t . The symbols represent data for the fluids considered (Ref. 15). The solid line represents Eq. (25) with the values of parameters given in Table II and the dashed line represents Eq. (3) (Ref. 5)

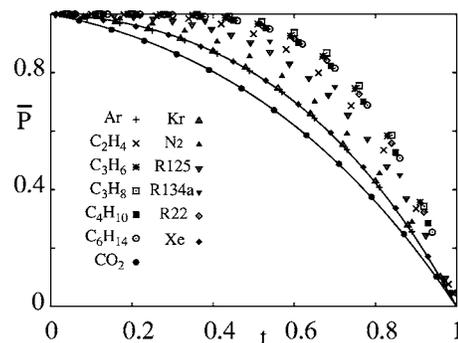


FIG. 3. Plot of the reduced SP \overline{P} [see Eq. (6)] vs the reduced temperature t . The symbols represent data for the fluids considered (Ref. 15) and the solid lines represent Eq. (25) with $\lambda=1$ and $b=0.271$ for CO_2 and with $\lambda=1$ and $b=0.065$ for noble gases.

IV. CONNECTION WITH EARLIER EMPIRICAL EQUATIONS

Table II shows that for the DCD, STSL, and SP one has $\lambda \approx b$ and $A'_\lambda \approx 1$. In this case, Eq. (25) becomes

$$\frac{\psi(T) - \psi_c}{\psi_t - \psi_c} \approx \left(\frac{1 - T/T_c}{1 - T_t/T_c} \right)^\lambda. \quad (26)$$

Empirical correlations of this type (using as reference the normal boiling point instead of the triple point) have been proposed for the temperature dependence of the DCD,¹⁸ EV,²² and STSL.²³ Furthermore, using Eq. (25), one obtains

$$A_\lambda \approx \frac{(\psi_t - \psi_c)}{(1 - (T_t/T_c))^\lambda}, \quad (27)$$

which provides an approximate value for the critical amplitude A_λ in terms of the critical exponent λ and the triple-point and critical-point values of the temperature and the corresponding thermodynamic property. For example, for the DCD of Xe one has $\psi_t = 2.682$ and $T_t/T_c = 0.557$, so that, taking $\lambda = 0.350$, Eq. (27) yields $A_\lambda = 3.57$. By fitting experimental data for the DCD of Xe near the critical point [$10^{-5} < |(T - T_c)/T_c| < 10^{-2}$] Estler *et al.*²⁴ obtain a critical exponent of 0.344 ± 0.003 and a critical amplitude of 3.51 ± 0.05 .

In 1985, Majer and Svoboda²⁵ compiled experimental values of EV for approximately 600 organic compounds, and found that for many of the substances the data could be represented by the function

TABLE II. Values of the parameters used in Eq. (25) for the different magnitudes studied. These values have been used to plot the corresponding curves in Fig. 1 and 2. The calculation of λ and b has been done by using a nonlinear fit procedure based on a Marquardt-Levenberg method. As a convergence criterion for the fit procedure we considered that the sum of the squared differences was less than 10^{-5} .

ψ	λ	b	$e^{\lambda-b} \approx A'_\lambda$
$\frac{\Delta\rho}{\rho_c}$	0.350	0.302	1.049
$\frac{\sigma}{p_c^{2/3} T_c^{1/3}}$	1.230	1.261	0.969
$\frac{\Delta H}{RT_c}$	0.380	0.371	1.009

$$\Delta H = A(1 - T_r)^\beta \exp(-\alpha T_r), \quad (28)$$

where A , β , and α are system-dependent parameters. Our Eq. (25) for the case of EV ($\psi_c=0$) becomes Eq. (28) with the obvious identification $\lambda = \beta$ and

$$A = \frac{\Delta H_t e^{(\lambda-b)/(1-T_t/T_c)}}{(1 - (T_t/T_c))^\lambda}, \quad (29)$$

$$\alpha = \frac{\lambda - b}{(1 - (T_t/T_c))}. \quad (30)$$

Hence, the parameters A and α of Eq. (28) are given in terms of our parameters λ and b , and the triple-point and critical-point data.

Finally, we would note that Eq. (20) can also provide a basis for Eq. (3) which was proposed by Meyra *et al.*⁵ for the EV. In particular, Eq. (20) can be written in the form

$$\bar{\psi}(t) = (1-t)^{\lambda + \frac{\sum_{n=1}^{\infty} a_n t^n}{\ln(1-t)}} = (1-t)^{\sum_{n=0}^{\infty} c_n t^n}, \quad (31)$$

where

$$c_0 = \lambda - a_1 = b, \quad (32)$$

$$c_1 = \frac{a_1}{2} - a_2, \quad (33)$$

$$c_2 = \frac{a_1}{6} + \frac{a_2}{2} - a_3, \dots \quad (34)$$

Truncation of Eq. (31) up to the first order in t yields

$$\bar{\psi}(t) = (1-t)^{c_0+c_1 t}, \quad (35)$$

which has the same form as the expression proposed by Meyra *et al.*,⁵ Eq. (3), with $c_0=Z_c$ and $c_1=Z_c^2$. Near the critical point, Eq. (35) becomes

$$\bar{\psi}(t) = (1-t)^{c_0+c_1 t} \quad (1-t \ll 1), \quad (36)$$

which compared with Eq. (21) gives $A'_\lambda=1$ and $\lambda=c_0+c_1$. Taking $Z_c=0.292$ one has $\lambda=0.377$ and $b=c_0=0.292$. The values of A'_λ and λ are in agreement with those given in Table II, but the value of b is smaller than that given in the table because the set of substances considered by Meyra *et al.* have values of b on the low side of the range considered in Table I, i.e., $b \sim 0.30$. This can be seen in Fig. 2 where we have also plotted Eq. (3) (dashed line). We also note that Eq. (35) is similar to the one proposed for the EV by Chueh and Swanson,²⁶ while Eq. (31) truncated at second order in t corresponds to the EV equation proposed by Guermouche and Vergnaud.²⁷

V. CONCLUSIONS

When some thermodynamic properties are converted to reduced form by using both critical- and triple-point values, the corresponding experimental data along the whole liquid-vapor coexistence curve reduce to a single curve for a wide class of fluids. We find this apparent universality in the difference of coexistence densities (DCD), in the surface tension of the saturated liquid (STSL), and, to a lesser degree, in

the enthalpy of vaporization (EV). In order to understand this behavior we proposed an equation that interpolates the temperature dependence of a given thermodynamic property between the neighborhood of the critical point and the triple point. Under certain circumstances, this equation reduces to some of the empirical correlations that have been proposed in the literature. For the above three thermodynamic properties we find that the proposed equation becomes a simple expression containing only two parameters, the critical-point exponent λ and the slope at the triple point b . Then, since for a given thermodynamic property λ can be considered as universal, there is universality along the whole coexistence curve for those substances for which b has nearly the same value. We also analyzed the saturation pressure (SP) as an example of a thermodynamic property that does not exhibit such universal behavior.

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²⁰ Taking into account the Clausius-Clapeyron equation, the critical amplitude for the EV can be obtained from the relationship $A_\lambda = \alpha_c Z_c A_\beta$, where α_c is the Riedel parameter, Z_c is the critical compressibility factor, and A_β is the critical amplitude for the DCD. Values for α_c and Z_c have been

taken from Ref. 2, p. 7.24. and Appendix A.

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