Applying a Low Temperature Limit of a Cubic Equation of State to Model Pure Component Phase Equilibrium

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Introduction

Equations of state may be used to calculate pure component vapor-liquid equilibrium properties such as vapor pressure, heat of vaporization, liquid density, and vapor density. The standard approach requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. The resulting equations are nonlinear and must be solved by numerical methods.

An alternative approach is applicable to cubic EOS such as the commonly used Soave-Redlich-Kwong and Peng-Robinson equations. Equilibrium properties may be explicitly expressed as power series in reduced temperature or related functions. These results are more convenient than numerical calculations, but the series diverge and become unbounded at low to moderate temperatures away from the critical point.

An alternative method was developed using a series expansion in a low temperature limit rather than the critical point limit. Although the limiting behavior itself was unphysical because it fell below the triple point of the substance, the expressions remained convergent over a very wide range of temperatures and they remained bounded over all temperatures from zero to the critical point. A second alternative method replaced the series expansions with closed form expressions which could be used up to reduced temperatures at least as high as 0.814. Dimensionless results for equilibrium properties such as vapor pressure and liquid density were determined as general expressions of the acentric factor of a substance. The deviations between these results and the exact equilibrium property predictions from the EOS were quantitatively characterized and found to be less than seven percent in one version of the second alternative method which combined a quadratic liquid density estimate with a vapor phase fugacity correction.

VLE from Cubic Equations of State

Cubic equations of state of the Van der Waals type are widely used in chemical engineering practice because they provide a reasonable balance between accuracy and simplicity. Two common examples are the Soave-Redlich-Kwong [1] and Peng-Robinson [2] equations, shown below as Eqs. (1) and (2),

$$P = \frac{RT}{V - b_{SRK}} - \frac{a_{SRK}(T)}{V(V + b_{SRK})} \tag{1}$$

$$P = \frac{RT}{V - b_{PR}} - \frac{a_{PR}(T)}{V(V + b_{PR}) + b_{PR}(V - b_{PR})} \tag{2}$$

In these equations, the attractive function $a_{EQ}(T)$ has the form

$$a_{EQ}(T) = a_{c,EQ}[1 + f_{EQ}(\omega)(1 - T_r^{1/2})]^2 \qquad (3)$$

with the critical value of

$$a_{c,EQ} = \frac{a_{0,EQ}R^2T_c^2}{P_c} \qquad (4)$$

and the acentric factor functions given by

$$f_{SRK}(\omega) = 0.480 + 1.574\omega - 0.176\omega^2 \qquad (5)$$
$$f_{PR}(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (6)$$

The occupied volume parameter b is given by

$$b_{EQ} = \frac{b_{0,EQ}RT_c}{P_c} \qquad (7)$$

Values of the dimensionless numerical constants in Eqs. (4) and (7) are $a_{0,SRK} = 0.42748$, $a_{0,PR} = 0.45724$, $b_{0,SRK} = 0.08664$, and $b_{0,PR} = 0.07780$.

Like many equations of state, SRK and PR may be used to calculate vapor pressure and other pure component vapor-liquid equilibrium properties. Doing this requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. Eqs. (8) and (9) give expressions for the pure component fugacity coefficient for SRK and PR.

$$\ln \phi_{SRK} = z - 1 - \ln z - \ln(1 - h) - \frac{a_{SRK}}{b_{SRK}RT}\ln(1 + h) \qquad (8)$$

$$\ln \phi_{PR} = z - 1 - \ln z - \ln(1 - h) - \frac{a_{PR}}{2\sqrt{2}b_{PR}RT}\ln\frac{1 + h(1 + \sqrt{2})}{1 + h(1 - \sqrt{2})} \qquad (9)$$

$$z = \frac{PV}{RT} \qquad (10)$$

$$h = \frac{b_{EQ}}{V} \qquad (11)$$

When an equilibrium state exists, Eq. (1) gives three real roots for volume from SRK. The smallest and largest of these are liquid and vapor volumes, respectively. The fugacity coefficients calculated by Eq. (8) will be equal when the liquid volume is substituted and when the vapor volume is substituted. For PR, Eqs. (2) and (9) are used. A numerical algorithm is required to solve either of these sets of nonlinear equations.

Power Series Methods for Cubic Equation VLE

A formal procedure [3] is available to express results for phase densities and vapor pressure of coexisting liquid and vapor phases as analytic power series in temperature. The approach begins by writing reduced deviation variables for phase densities ($\Delta\rho^L$ and $\Delta\rho^V$) and temperature (ΔT) about the critical point. These variables are defined as

$$\Delta M = M_r - 1 = \frac{M - M_c}{M_c} \tag{12}$$

with M representing either ρ^L, ρ^V, or T. The resulting formal power series are

$$P_r = \sum_{j=0}^{\infty} A_j (\Delta T)^j \tag{13}$$

$$\Delta\rho^L = \sum_{i=1}^{\infty} B_i (-\Delta T)^{i/2} \tag{14}$$

$$\Delta\rho^V = \sum_{i=1}^{\infty} (-1)^i B_i (-\Delta T)^{i/2} \tag{15}$$

After equilibrium constraints are applied to these series, the coefficients A_j and B_i are observed to be functions of the acentric factor function $f_{EQ}(\omega)$ which depend upon the cubic EOS being applied. They are substance-dependent since they contain the acentric factor function. For SRK and PR, A_j is given by a polynomial of degree j in the acentric factor function, B_i is given by a polynomial of degree (i-1) in the acentric factor function for even i, and by a similar polynomial multiplied by the square root of (1+ $f_{EQ}(\omega)$) for odd i. Expressions for these polynomials have been tabulated. [4,5]

The utility of this method stems from the convenience of direct computation of coexisting phase properties without need for auxiliary equilibrium criteria such as fugacities. The weaknesses of the method arise from being based upon a series expansion about the critical point. In practice, the infinite series given by Eqs. (13) to (15) must be truncated. Few terms are required near the critical point, but this is the situation where cubic EOS are least accurate. At moderately high or moderate temperatures, where the equations have reasonable accuracy, many series terms are needed to prevent truncation error. The magnitude of truncation error also depends upon the property (phase density or vapor pressure) and varies with acentric factor. In general, truncation errors are largest for vapor density and smallest for liquid density, they are larger for the PR equation as compared to SRK, and they increase with increasing acentric factor.

Low Temperature Limit Methods for Cubic Equation VLE

An alternative approach for prediction of pure component coexisting phase properties was proposed to overcome some of the shortcomings of the critical point power series, specifically the large truncation errors and subsequent poor convergence at low to moderate temperatures. This new approach utilized expressions for density and vapor pressure that

were asympotically correct in a low temperature limit yet still converged well at moderate to high temperatures. Note that the zero temperature limit used is an unphysical limit from the standpoint of VLE, as liquid behavior does not persist below the triple point which typically falls near a reduced temperature of 0.3 to 0.4. In the best case, the existing series about the critical point did not extrapolate accurately below a reduced temperature of approximately 0.58, and even that accuracy required j = 13 in the series expansion for SRK.

For the SRK equation, a relationship between reduced vapor pressure and reduced temperature was found in the mathematical (unphysical) zero temperature limit as the following truncated series in one-half powers of reduced temperature. [6]

$$\ln P_r = \frac{C_1}{T_r} + \frac{C_2}{T_r^{1/2}} + C_3 + C_4 T_r^{1/2} + C_5 T_r \tag{16}$$

$$C_1 = -\frac{a_{0,SRK}(1 + f_{SRK}(\omega))^2 \ln 2}{b_{0,SRK}} \tag{17}$$

$$C_2 = \frac{2a_{0,SRK} f_{SRK}(\omega)(1 + f_{SRK}(\omega)) \ln 2}{b_{0,SRK}} \tag{18}$$

$$C_3 = \ln \frac{a_{0,SRK}(1 + f_{SRK}(\omega))^2}{2b_{0,SRK}} - \frac{a_{0,SRK}(f_{SRK}(\omega))^2 \ln 2}{b_{0,SRK}} - \ln b_{0,SRK} \tag{19}$$

$$C_4 = -\frac{4 f_{SRK}(\omega)}{1 + f_{SRK}(\omega)} \tag{20}$$

$$C_5 = -\frac{2b_{0,SRK}}{a_{0,SRK}(1 + f_{SRK}(\omega))^2} + \frac{3(f_{SRK}(\omega))^2}{(1 + f_{SRK}(\omega))^2} \tag{21}$$

This result was derived by substituting an expression for reduced liquid density ρ_r' given by Eq. (22) into Eq. (8) to evaluate liquid fugacity coefficient. (The prime in this definition is used to emphasize that this is not the standard reduced density determined by dividing by the critical density.) A value of unity was assigned to the vapor fugacity coefficient, reflecting nearly perfect adherence to the ideal gas law at the extremely low vapor pressures corresponding to a low temperature limit, and liquid and vapor fugacity coefficients were equated to give Eqs. (16) to (21).

$$\rho_r' \equiv b_{SRK}\rho = 1 - \frac{2b_{0,SRK}}{a_{0,SRK}(1 + f_{SRK}(\omega))^2} T_r - \frac{4 f_{SRK}(\omega)b_{0,SRK}}{a_{0,SRK}(1 + f_{SRK}(\omega))^3} T_r^{3/2} \tag{22}$$

Figure 1 shows results when vapor pressure predicted by Eq. (16) is compared to the exact result from the SRK equation. The curves plotted in Figure 3 represent various acentric factors. Since the coefficients in Eq. (16) were fit in the low temperature limit, the deviation between the predictions and the exact SRK result went to zero in that limit. Behavior at increasing temperatures was interesting. Although no additional corrections were made to the fit of the equation, the zero temperature limit equation was capable of tracking the exact vapor pressure from the SRK equation within an order of magnitude; in fact, within a factor of two, over the entire temperature range from zero to the critical point. This was unlike the behavior

observed with the truncated critical point series of Eq. (13), where the deviation caused by truncation error increased by polynomial or exponential order away from the critical point.

Results analogous to Eqs. (16) to (22) were also determined for the Peng-Robinson equation. Details of those results and additional descriptions of the method used to derive these results for both SRK and PR will be given in a subsequent publication.
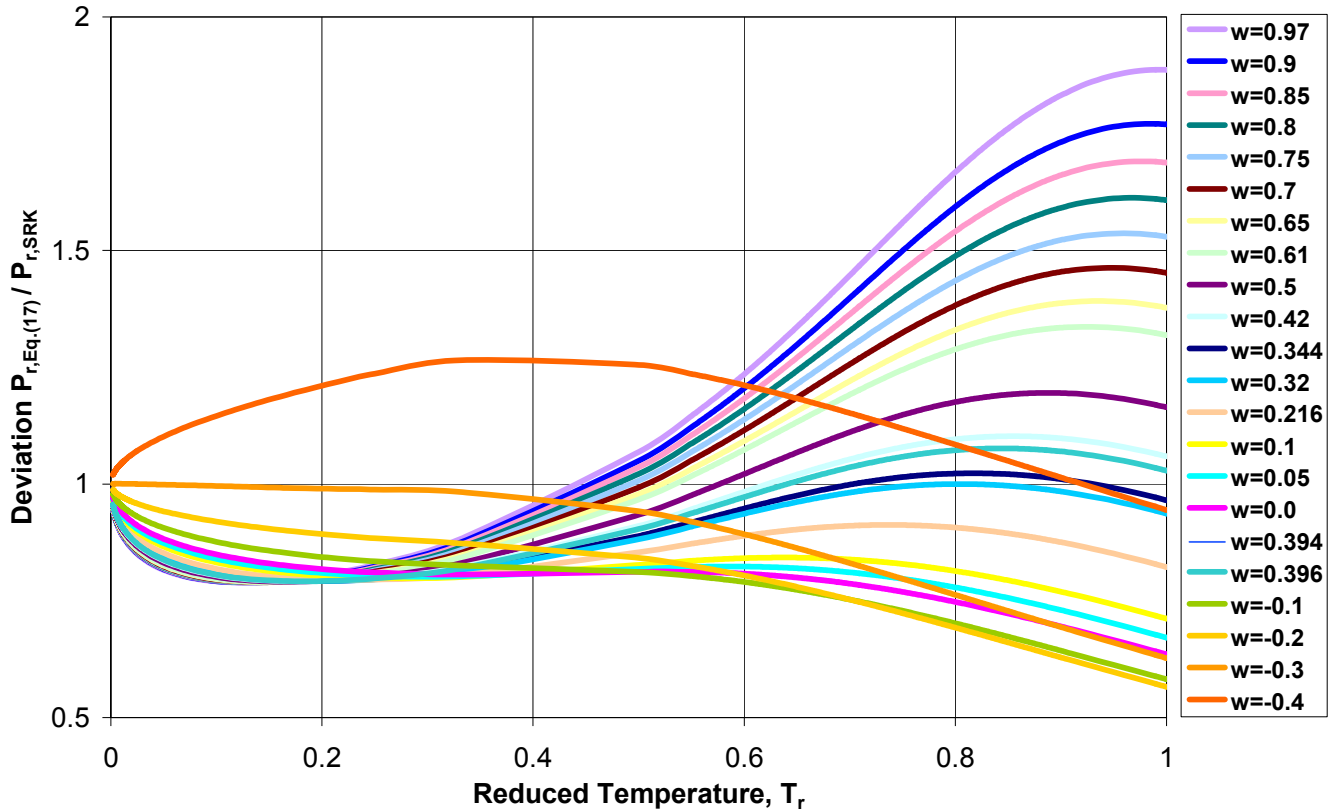

Figure 1. Deviation Ratio Between Eq. (16) and Exact SRK Vapor Pressure.

It was noted that a principal source of the deviations shown in Figure 1 was the truncation error in the prediction of liquid density by Eq. (22). To improve the predictions of the method, an alternative approach was developed for predicting liquid density. A cubic EOS such as SRK or PR was written in dimensionless variables using the critical point to nondimensionalize temperature and pressure in the standard way, but nondimensionalizing density by multiplying it by the parameter b of the EOS as was done in Eq. (22). The result for the SRK equation is shown as Eq. (23), where α_{SRK} refers to the second factor in Eq. (3) which is shown here as Eq. (24).

$$P_r - \frac{T_r}{b_{0,SRK}}\rho_r' + (\frac{a_{0,SRK}\alpha_{SRK}}{b_{0,SRK}^2} - \frac{T_r}{b_{0,SRK}} - P_r)\rho_r'^2 - \frac{a_{0,SRK}\alpha_{SRK}}{b_{0,SRK}^2}\rho_r'^3 = 0 \qquad (23)$$

$$\alpha_{SRK} = [1 + f_{SRK}(\omega)(1 - T_r^{1/2})]^2 \tag{24}$$

In the low temperature limit, it was observed that P_r approaches zero exponentially as T_r decreases. Applying this observation to Eq. (23), the P_r terms were neglected to give a cubic equation with no constant term. By factoring out the common factor of ρ_r' from each term, a low temperature limit of the cubic EOS was written as a quadratic equation, Eq. (25).

$$\frac{T_r}{b_{0,SRK}} + (\frac{a_{0,SRK}\alpha_{SRK}}{b_{0,SRK}^2} - \frac{T_r}{b_{0,SRK}})\rho_r' - \frac{a_{0,SRK}\alpha_{SRK}}{b_{0,SRK}^2}\rho_r'^2 = 0 \tag{25}$$

$$\rho_r' = -\frac{T_r b_{0,SRK}}{2a_{0,SRK}\alpha_{SRK}} + \frac{1}{2} + \sqrt{\left(\frac{T_r b_{0,SRK}}{2a_{0,SRK}\alpha_{SRK}}\right)^2 - 3\left(\frac{T_r b_{0,SRK}}{2a_{0,SRK}\alpha_{SRK}}\right) + \frac{1}{4}} \tag{26}$$

Eq. (25) could be solved easily by the quadratic formula for two roots of reduced density ρ_r'. The larger of these was an approximation of the liquid reduced density, shown as Eq. (26) and the smaller was an approximation of the unphysical middle root from the cubic EOS. The vapor reduced density root disappeared when the common factor of ρ_r' was factored from Eq. (23). This factoring process was equivalent to identifying an additional root of ρ_r' equal to zero, which would be the ideal gas limit at the extremely low pressures of the zero temperature limit. Note that the novelty was not merely in replacing a cubic polynomial with a quadratic polynomial as both may be solved for a closed form, but rather in eliminating P_r from the equation so that only one degree of freedom remained instead of two.

The same steps used in deriving Eqs. (16) to (21) from Eq. (8) were then applied, except that Eq. (26) was used to represent reduced liquid density instead of Eq. (22). This gave a relatively simple closed form expression for P_r.

$$P_r = \frac{a_{0,SRK}\alpha_{SRK}\rho_r'^2}{eb_{0,SRK}^2(1 + \rho_r')^{(1 + a_{0,SRK}\alpha_{SRK}/T_r b_{0,SRK})}} \tag{27}$$

The results of Eq. (27) had several interesting characteristics. They did converge asymptotically to the exact vapor pressures generated by a numerical algorithm in the low temperature limit. At higher temperatures, the deviation between Eq. (27) and the exact values was frequently less than for the more mathematically complex model given by Eqs. (16) to (21), especially for large values of the acentric factor; however, Eq. (27) could not be used beyond the reduced temperature where the discriminant (the quantity under the square root) in Eq. (26) became zero. This occurred for reduced temperatures between 0.814 (for an acentric factor of -0.4) to 0.94 (for an acentric factor of +0.97). Observed deviations were always negative, meaning that Eq. (27) underpredicted the exact SRK result, with the maximum negative deviation being 32 percent, occurring when the discriminant was zero.

One of the most interesting and unexpected observations was that the deviation between Eq. (27) and the exact SRK vapor pressure predictions, which appeared to be a function of two parameters (T_r and ω), could be written as a function of a single parameter.

This parameter was an expression containing both T_r and ω and it was identified as the discriminant of Eq. (26). This result was verified empirically and a master graph of the deviation versus the discriminant was produced, shown as Figure 2. The combination of this figure with Eqs. (26) and (27) allows essentially exact estimation of an SRK vapor pressure at any reduced temperature below the point at which the discriminant of Eq. (26) becomes zero.

Results analogous to Eqs. (23) to (27) were also determined for the Peng-Robinson equation, including the characteristics discussed above. Again, the maximum negative deviation observed was 32 percent. Details of those results and additional descriptions of the method used to derive these results for both SRK and PR will be given in a subsequent publication.
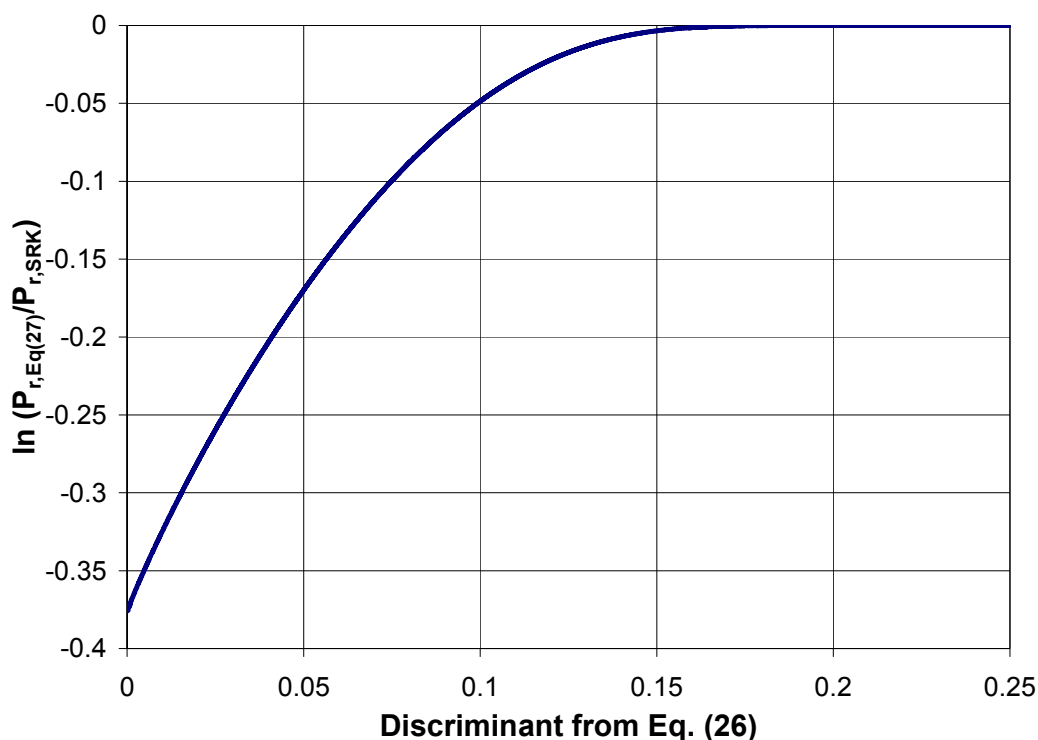

Figure 2. Log Deviation Ratio Between Eq. (27) and Exact SRK Vapor Pressure.

Work continues on characterizing the empirical function of Figure 2 with a functional expression and understanding the mathematical basis for the empirical result that the deviation between Eq. (27) and the exact SRK vapor pressure depends on the single parameter which is the discriminant of Eq. (26).

In deriving the previous results, the vapor phase fugacity coefficient was always assumed equal to unity (ln $\varphi^V = 0$). An additional enhancement to the method was made by making a first order correction. The SRK equation was expressed in a virial expansion and the second virial coefficient term was used to correct the vapor fugacity coefficient. When the liquid and vapor fugacity coefficients were equated, the result was a quadratic equation which could be directly solved for reduced pressure P_r.

$$\left(\frac{a_{0,SRK} \alpha_{SRK}}{T_r^2} - \frac{b_{0,SRK}}{T_r} \right) P_r^2 - P_r + \frac{a_{0,SRK} \alpha_{SRK} \rho_r'^2}{e b_{0,SRK} (1 + \rho_r')^{(1 + a_{0,SRK} \alpha_{SRK} / T_r b_{0,SRK})}} = 0 \qquad (28)$$

As was the case with Eq. (27) above, the value of reduced liquid density ρ_r' from Eq. (26) is used in evaluating Eq. (28). Like Eq. (27), Eq. (28) asymptotically converged in the low temperature limit to the exact SRK vapor pressure. Furthermore, the deviations between vapor pressures found by solving Eq. (28) and exact SRK vapor pressures were quite small even at higher temperatures, less than seven percent for all acentric factors between -0.4 and +0.97. As with Eq. (27), the method could not be used at reduced temperatures very close to the critical point where the discriminant in Eq. (26) became negative. Unlike Eq. (27), the deviations between Eq. (28) and exact SRK vapor pressures could not be expressed as a function of the discriminant as a single parameter, but had to be given as functions of the two parameters T_r and ω.

Results analogous to Eqs. (28) were also determined for the Peng-Robinson equation, with the maximum negative deviation observed being 1.4 percent. Details of those results and additional descriptions of the method used to derive these results for both SRK and PR will be given in a subsequent publication.

Conclusions

Methods for explicit estimation of vapor pressure from cubic EOS were presented. The methods relied upon expressions which were asymptotically correct in the zero temperature limit. These approaches were shown to reproduce, with reasonable accuracy, the vapor pressure determined by combining the EOS with a phase equilibrium constraint such as fugacity. The methods were applicable for reduced temperatures from zero up to at least 0.814 and in some cases as high as 0.94. Deviations from the exact SRK vapor pressure were less than 32 percent for an approach which used a quadratic density estimate and less than 7 percent for a modified approach which added a vapor phase fugacity correction. The methods also were applicable to the PR equation with similar accuracy.

Acknowledgements

Nomenclature

A_j temperature coefficients in Eq. (13) for reduced pressure
$a_{EQ}(T)$ energy parameter in attractive term
$a_{c,EQ}$ energy parameter in attractive term at the critical point
$a_{0,EQ}$ dimensionless numerical coefficient of energy parameter

B_i temperature coefficients in Eqs. (14) and (15) for reduced density deviation variables
b_{EQ} excluded volume parameter in equation of state
$b_{0,EQ}$ dimensionless numerical coefficient of excluded volume parameter
C_i coefficients in Eq. (16), vapor pressure equation at low temperature limit
$f_{EQ}(\omega)$ quadratic function of acentric factor
h ratio of excluded volume parameter to molar volume
M general thermodynamic state property (T, ρ^L or ρ^V) in Eq. (12)
P absolute pressure
R gas constant
T absolute temperature
V molar volume
z compressibility

Greek letters

ΔM reduced deviation variable of state property M (T, ρ^L or ρ^V) defined by $M_r - 1$
ρ molar density
ρ_r' reduced molar density of liquid defined by convention of Eq. (22)
φ_{EQ} fugacity coefficient for equation of state
ω acentric factor

Subscripts

c   critical (temperature, pressure, or molar density)
EQ   parameter or coefficient applying to equation of state EQ (SRK or PR)
r   reduced (temperature, pressure, or molar density)

Superscripts

L   liquid (molar density or molar volume)
V   vapor (molar density or molar volume)

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