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Reduced departure functions for pure substances described by Padé representations of two-parameter equations of state

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Abstract. The virial series expansions of the pressure corresponding to the reduced two-parameter Redlich-Kwong, and Peng-Robinson equations of state for real gases are represented by means of Padé approximants. The Padé representations are then employed to determine the reduced departure functions for pure component systems described by the two model equations.

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1. Introduction

The need for accurate information on the thermodynamic properties and the compressibilities of pure gases at high pressures has traditionally been of interest mainly in industrial processes [1]. As is well known, there are several techniques available for obtaining information on the thermodynamic properties and compresibilities of gases. In this article we present still another method, namely, the one employing the analytical equations of state for the gases, the theorem of corresponding states, and the virial series expansion for the pressure. One advantage of the present treatment is that being expressible in terms of analytical functions, the thermodynamic properties of a pure material may be calculated for a very wide range of conditions, and is *not* directly dependent upon the compressibility data of the gas. The work reported here employs the two-parameter equations of state proposed by Redlich and Kwong [2], and Peng and Robinson [3], for the determination of the analytical expressions for the differences between real-gas and ideal-gas thermodynamic properties.

The virial series expansions of the pressure are useful only for relatively small values of the density. These expressions do not permit successful extrapolation, especially to *higher* densities and lower temperatures. There are, however, means of extrapolating the low-density expansion of the pressure so as to encompass higher densities. We have chosen to employ a Padé approximant representation for the virial series for the pressure, which is valid beyond the radius of convergence of the original truncated virial equation that it represents [4]. The Padé extrapolant form of the reduced pressure will then be employed in a thermodynamically consistent fashion to determine the reduced departure functions for pure substances described by the Redlich-Kwong and Peng-Robinson relations.

2. The model equations

Besides the celebrated analytical equation of state for gases proposed by van der Waals there are in the literature several other two-parameter relations in use. Among these mention should be made of those associated with the names of Berthelot [5], Dieterici [6], Lorentz [7], Redlich and Kwong, and Peng and Robinson. The motivation for the authors' choice of the last two equations of this set hinges primarily on the fact that the other relations are each less accurate and more complicated in form than the van der Waals equation [8,9]. Furthermore, a comparison of a large number of two-parameter equations of state for gases performed nearly two decades ago reports the Redlich and Kwong relation as the most accurate [10]. Results of an earlier examination on the performance of equations of state for gases [11] indicate that the two-parameter Redlich-Kwong equation is "at least as good" as the five parameter Beattie-Bridgman relation and the eight-parameter Benedict-Webb-Rubin equation. The Redlich-Kwong relation and the more recent equation of state proposed by Peng and Robinson have gained popularity among the chemical and process engineers in high-pressure work. The well-known Redlich-Kwong equation of state reads

$$\frac{P}{k_B T} = \frac{\rho}{1-b\rho} - \frac{a\rho^2}{k_B T^{3/2}(1+b\rho)} \tag{1}$$

and the relationship proposed by Peng and Robinson can be written as

$$\frac{P}{k_B T} = \frac{\rho}{1-b\rho} - \frac{a\rho^2}{k_B T(1+2b\rho-b^2\rho^2)} \tag{2}$$

In Eqs. (1) and (2) P denotes the total pressure, T represents the absolute temperature, k_B is Boltzmann's constant, and ρ stands for number density, $\rho = N/V$, N being the total number of particles and V the volume of the container. The quantities a and b in Eqs. (1) and (2) are phenomenological positive constants and are *different* for each semiempirical equation of state. In the study here reported the parameter "a" employed in Eq. (2) is taken to be independent of both the reduced temperature and the acentric factor; in fact, for convenience of computation it is assumed here that "a" is a constant equal to the value that the parameter attains in the original Peng-Robinson relation at the critical temperature. In Eqs. (1) and (2) the covolume "b" is, to a first approximation, four times the actual volume of the molecules, if these are assumed to be hard spheres.

Expressing the pressure, density, and temperature in reduced form

$$P_r \equiv \frac{P}{P_c}, \qquad \rho_r \equiv \frac{\rho}{\rho_c}, \qquad T_r \equiv \frac{T}{T_r} \tag{3}$$

and employing the dimensionless parameter $\alpha = b\rho_c$ permits writing Eqs. (1) and (2) as

$$P_{RK}(\rho_r) = \frac{\rho_r T_r}{Z_{RK}(1-\alpha\rho_r)} - \frac{(1+\alpha)^3\rho_r^2}{2\alpha T_r^{1/2}(1+\alpha\rho_r)} \tag{4}$$

and

$$P_{PR}(\rho_r) = \frac{\rho_r T_r}{Z_{PR}(1-\alpha\rho_r)} - \frac{(\alpha^2-2\alpha-1)^3\rho_r^2}{\alpha(\alpha^3+3\alpha^2-3\alpha+3)(\alpha^2\rho_r^2-2\alpha\rho_r-1)} \tag{5}$$

We have employed the letter subscripts RK and PR to indicate the Redlich-Kwong and the Peng-Robinson systems, respectively.

Whereas in Eq. (4) $\alpha = 0.259921$, the value to be used for α in Eq. (5) is [1] $\alpha = 0.253076$. To keep the notation uncluttered the subscript r in the symbol for the reduced pressure has been omitted in Eqs. (4) and (5). Clearly, both of these equations can be readily simplified by substituting in them the corresponding values of α. We have chosen to leave all equations in this paper in algebraic form as this practice would help in visualizing differences and similarities between corresponding functions in the two models employed. In the dimensionless representation of the equations of state given by Eqs. (4) and (5), Z_{RK} and Z_{PR} denote the compressibility factor of a Redlich-Kwong and a Peng-Robinson system respectively; their numerical values are [1] $Z_{RK} = 1/3$, and $Z_{PR} = 0.17149$.

3. Padé approximations for the models

Straightforward expansion of Eq. (4) about $\rho_r = 0$ as an infinite virial series and extrapolation of the ensuing series to positive ρ_r by means of a Padé approximant renders the equation

$$P_{RK}(\rho_r) = \frac{T_r\rho_r}{Z_{RK}}\left[1 + \sum_{k=1}^{\infty} B_{k+1}^{RK}(T_r)\rho_r^K\right]$$

$$\hat{=} \left(\frac{T_r \rho_r}{Z_{RK}}\right) \left[\frac{L}{M}\right] (\rho_r). \tag{6}$$

In Eq. (6) we must take [1] $\alpha = .259921$. The quantity $B^{RK}(T_r)$ represents the $(k+1)$–th reduced virial coefficient of a Redlich-Kwong system, and is given by the functional relation

$$B_{k+1}^{RK}(T_r) = \alpha^k \left[1 + \frac{(-1)^k}{3\alpha^2 T_r^{3/2}}\right], \qquad k = 1, 2, 3, 4, \ldots \tag{7}$$

For a Peng-Robinson system it can be easily verified that

$$P_{PR}(\rho_r) = \frac{T_r \rho_r}{Z_{PR}} \left[1 + \sum_{k=1}^{\infty} B_{k+1}^{PR}(T_r) \rho_r^k\right] \hat{=} \left(\frac{T_r \rho_r}{Z_{PR}}\right) \left[\frac{L}{M}\right] (\rho_r) \tag{8}$$

where the reduced virial coefficients are given by the expression

$$B_{k+1}^{PR}(T_r) = \alpha^k \left[1 + \frac{D_k (1 + 2\alpha - \alpha^2)^3}{(2\alpha^3 + 3\alpha^2 + 1)(1 - \alpha)^3 T_r}\right], \qquad k = 1, 2, 3, 4, \ldots \tag{9}$$

Again, in Eq. (8) $\alpha = 0.253076$. Because of the way the parameter "a" has been defined in this paper the effect of the acentric factor on B^{PR} is not included in Eq. (9). The D_k's appearing in Eq. (9) are simply the coefficients in the MacLaurin expansion of the function $F(x) = (x^2 - 2x - 1)^{-1}$. For ready reference for calculations the first twelve values of D_k are presented here: $-1, 2, -5, 12, -29, 70, -169$, $408, -985, 2378, -5741$, and 13860.

4. Calculations of the reduced departure functions

The advantage of virial series expansions, such as those given by Eqs. (6) and (8), lies not so much in their capability to predict compressibility factors as in their usefulness in calculating thermodynamic properties. Starting with basic thermodynamic relations given in any number of textbooks [1] it can be readily shown that the reduced Helmholtz free energy departure $(\Delta A)_r$, entropy departure $(\Delta S)_r$ and enthalpy departure $(\Delta H)_r$ functions of a gas from the *ideal-gas state* are given by:

$$(\Delta A)_r = \int_0^{\rho_r} d\rho_r \left[\frac{P_r(\rho_r, T_r)}{\rho_r^2} - \frac{T_r}{\rho_r Z_c}\right] + \frac{T_r}{Z_c} \ln\left(\frac{\rho_r}{\rho_r^0}\right) \tag{10}$$

$$(\Delta S)_r = -\frac{\partial}{\partial T_r}\int_0^{\rho_r} d\rho_r \left[\frac{P_r(\rho_r, T_r)}{\rho_r^2} - \frac{T_r}{\rho_r Z_c}\right] - \frac{1}{Z_c}\ln\left(\frac{\rho_r}{\rho_r^0}\right) \tag{11}$$

and

$$(\Delta H)_r = (\Delta A)_r + T_r(\Delta S)_r + \frac{T_r}{Z_c}(Z-1) \tag{12}$$

where ρ_r^0 is the reduced density of a reference state, and Z and Z_c are the compressibility factors at an arbitrary volume, temperature, and pressure, and at the critical point, respectively. Substitution of either Eq. (6) or (8) into Eqs. (10) through (12) allows immediate evaluation of the integrals. The results are

$$(\Delta A)_r = \frac{T_r}{Z_c}\sum_{k=1}^{\infty}\frac{B_{k+1}^*(T_r)}{k}\rho_r^k - \frac{T_r}{Z_c}\ln\Big[1 + \sum_{k=1}^{\infty} B_{k+1}^*(T_r)\rho_r^k\Big] \tag{13}$$

$$(\Delta S)_r = -\frac{1}{Z_c}\sum_{k=1}^{\infty}\frac{\rho_r^k}{k}\left(1 + T_r\frac{\partial}{\partial T_r}\right)B_{k+1}^*(T_r) + \frac{T_r}{Z_c}\ln\Big[1 + \sum_{k=1}^{\infty} B_{k+1}^*(T_r)\rho_r^k\Big] \tag{14}$$

and

$$(\Delta H)_r = \frac{T_r}{Z_c}\sum_{k=1}^{\infty}\rho_r^k\Big(1 - \frac{T_r}{k}\frac{\partial}{\partial T_r}\Big)B_{k+1}^*(T_r) \tag{15}$$

Other departure functions can be readily obtained from Eq. (13). Eqs. (13)-(15) are useful even if only a limited number of virial coefficients is known, such as in the case of the Epstein equation [12].

An accurate alternate approach for evaluating the simple-fluid reduced departure functions is to employ the Padé representations for each of the virial expansions corresponding to the Redlich-Kwong or Peng-Robinson relations in Eqs. (10) through (12). This method will now be pursued. We begin by writing the Padé representation of the reduced Redlich-Kwong pressure:

$$P_{RK}(\rho_r) = \frac{T_r\rho_r}{Z_{RK}}\Big(\frac{1 + n_1\rho_r + n_2\rho_r^2}{1 + d_1\rho_r + d_2\rho_r^2}\Big) \tag{16}$$

Numerical values of the Padé coefficients in Eq. (16) for several values of the reduced temperature are found in Table I. Substituting Eq. (16) in Eq. (10) and integrating yields the following expression for the reduced Helmholtz free energy:

$$(\Delta A)_r = \frac{T_r}{d_2 Z_{RK}}\Big[F\ln|1 - \frac{\rho_r}{\rho_1}| + G\ln|1 - \frac{\rho_r}{\rho_2}| + \frac{T_r}{Z_{RK}}\ln\Big(\frac{\rho_r T_r}{P_{PK} Z_{RK}}\Big)\Big] \tag{17}$$

[2/2]	$T_r = 0.5$	$T_r = 0.75$	$T_r = 0.9$
n_1	−3.367369	−1.714526	−1.242091
n_2	0.942809	0.513200	0.390405
d_1	...	...	...
d_2	−0.067559	−0.067559	−0.067559

TABLE I. Numerator and denominator polynomial coefficients of the $[2/2](\rho_r)$ Padé approximant based on the Redlich-Kwong virial expansion corresponding to the reduced subcritical temperatures $T_r = 0.5, 0.75, \text{and} 0.9$.

[2/3]	$T_r = 0.5$	$T_r = 0.75$	$T_r = 0.9$
n_1	−2.468689	−1.477075	−1.146537
n_2	0.688815	0.437861	0.354209
d_1	0.253076	0.253076	0.253076
d_2	−0.192143	−0.192143	−0.192143
d_3	0.016209	0.016209	0.016209

TABLE II. Numerator and denominator polynomial coefficients of the $[2/2](\rho_r)$ Padé approximant based on the Peng-Robinson virial expansion corresponding to the reduced subcritical temperatures $T_r = 0.5, 0.75$, and 0.9.

where the auxiliary quantities F and G are defined by

$$F = \frac{n_1\rho_1 + 1 - n_2/d_2}{\rho_1(\rho_1 - \rho_2)}, \qquad G = \frac{n_1\rho_2 + 1 - (n_2/d_2)}{\rho_2(\rho_2 - \rho_1)} \tag{18}$$

and ρ_1, and ρ_2 are the poles of Eq. (16) for $d_1 = 0$, *i.e.*, $\rho_1 = \rho_2 = 3.847323$.

From the defining Eq. (11) and the result given by Eq. (17) it can be deduced that the reduced departure function for the entropy for a Redlich-Kwong system is

$$(\Delta S)_r = -\frac{1}{d_2 Z_{RK}}\Big[F \ln|1 - \frac{\rho_r}{\rho_1}| + G \ln|1 - \frac{\rho_r}{\rho_2}| - \frac{1}{Z_{RK}} \ln\Big(\frac{\rho_r T_r}{P_{PK} Z_{RK}}\Big)\Big] \tag{19}$$

Insertions of Eqs. (17) and (19) in Eq. (12) gives at once

$$(\Delta H)_r = \frac{T_r}{Z_{RK}}\Big[\frac{Z_{RK}P_{RK}}{\rho_r T_r} - 1\Big] \tag{20}$$

or, employing the Padé representation for the pressure given by Eq. (16)

$$(\Delta H)_r = \frac{T_r}{Z_{RK}}\Big[\frac{1 + n_1\rho_r + n_2\rho_r^2}{1 + d_2\rho_r^2} - 1\Big] \tag{21}$$

As usual, all other thermodynamic departure functions can be obtained from Eq. (17).

For a particular value of T_r the reduced virial coefficients are evaluated employing Eq. (7). Once these values are known the Padé $[2/2](\rho_r)$ for $P_{PR}(\rho_r)$, must be formed. A formula to achieve this, obtained using the algebraic manipulation computer system MACSYMA [13] is given in the Appendix. The roots of the denominator of Eq. (16) are easily found as the solutions of a quadratic equation in the reduced density, and the values of the auxiliary quantities F and G can be readily calculated. For a given value of the reduced density the departure function for the Helmholtz free energy can be evaluated. Minicomputers and programmable calculators are particularly helpful if a table of values of $(\Delta A)_r$ for several values of ρ_r at a particular value of T_r is desired. The numerical evaluations of $(\Delta S)_r$ and other departure functions are similarly easy to perform.

The above procedure can, of course, be repeated for the evaluation of the reduced departure functions for a Peng-Robinson system. However, the algebraic details of the solution are tedious enough to be distracting here and we will be content presenting the final results:

$$P_{PR}(\rho_r) = \frac{T_r\rho_r}{Z_{PR}}\frac{(1+n_1\rho_r+n_2\rho_r^2)}{(1+d_1\rho_r+d_2\rho_r^2+d_3\rho_r^3)} \tag{22}$$

$$\begin{aligned}(\Delta A)_r &= \frac{T_r}{d_3 Z_{PR}}\Big[B\ln|1-\frac{\rho_r}{\rho_1}|+C\ln|1-\frac{\rho_r}{\rho_2}|+D\ln|1-\frac{\rho_r}{\rho_3}|\Big] \\ &\quad + \frac{T_r}{Z_{PR}}\ln\Big(\frac{\rho_r T_r}{P_{PR}Z_{PR}}\Big)\end{aligned} \tag{23}$$

$$\begin{aligned}(\Delta S)_r &= -\frac{T_r}{d_3 Z_{PR}}\Big[B\ln|1-\frac{\rho_r}{\rho_1}|+C\ln|1-\frac{\rho_r}{\rho_2}|+D\ln|1-\frac{\rho_r}{\rho_3}|\Big] \\ &\quad - \frac{1}{Z_{PR}}\ln\Big(\frac{\rho_r T_r}{P_{PR}Z_{PR}}\Big)\end{aligned} \tag{24}$$

and

$$(\Delta H)_r = \frac{T_r}{Z_{PR}}\Big[\frac{1+n_1\rho_r+n_2\rho_r^2}{1+d_1\rho_r+d_2\rho_r^2+d_3\rho_r^3}-1\Big] \tag{25}$$

In Eqs. (23) and (24) the auxiliary quantity B is defined by

$$B = \frac{n_2\rho_1^2+n_1\rho_1+1}{\rho_1(\rho_1-\rho_2)(\rho_1-\rho_3)} \tag{26}$$

The auxiliary quantities C and D are readily obtained by simply interchanging ρ_1 and ρ_2, and ρ_1 and ρ_3, in Eq. (26) respectively. Notice that B, C, and D depend implicity on the reduced temperature through the Padé coefficients.

The poles of the $[2/3](\rho_r)$ approximant given by Eq. (22) are found employing any of the several root finder algorithms from the open literature. The results are $\rho_1 = 3.951314$, $\rho_2 = -1.636713$, and $\rho_3 = 9.539461$. Since the procedure to obtain the numerical results for the several departure functions in the present case is identical to that outlined for the Redlich-Kwong case it will not be repeated here.

5. Discussion

Padé approximants for the reduced pressure of real gases independently described by the two-parameter Redlich-Kwong and Peng-Robinson equations of state have been formed. These relatively simple representations for the reduced pressure have been consistently employed in the derivation of analytical expressions for several reduced departure functions of interest in chemical and process engineering. For each value of the reduced temperature a set of Padé coefficients must be calculated. All reduced departure functions are then deduced from that single Padé representing the reduced pressure, by analytical integration and differentiation thereby satisfying the thermodynamic consistency requirement. The convenience of machine computation outweighs the preparatory work of the user in obtaining the Padé coefficients even in moderately frequent application.

From the prescription given by Eqs. (7) and (9) it is seen that the reduced virial coefficients for the Redlich-Kwong and Peng-Robinson relations are *explicit* functions of the reduced temperature T_r. The temperature-derivative expressions of the reduced virial coefficients needed in Eqs. (14) and (15) for calculating the isothermal changes in $(\Delta S)_r$ and $(\Delta H)_r$ can then be found analytically. This suggests a third possibility of computing reduced departure functions. Indeed, Padé approximants of the same degree in both L and M could be constructed to represent all series expansions in Eqs. (13) through (15). It appears that there are no reliable *a priori* rules for selecting between the approach presented in this paper for obtaining departure functions, and the method just described. The calculations involved in the latter method have not been pursued here, and the work is left as an open problem for study.

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Appendix

Given the function

$$F(x) = 1 + f_1 x + f_2 x^2 + f_3 x^3 + f_4 x^4 + \cdots \tag{A1}$$

the analytical expression for the Padé $[2/2](x)$ is

$$[2/2](x) = \frac{P(x)}{Q(x)} \tag{A2}$$

where

$$\begin{aligned} P(x) = {} & (f_1 f_3 - f_2^2) + (f_1^2 f_3 + f_2 f_3 - f_1 f_4 - f_1 f_2^2)x \\ & + (f_2 f_4 - f_1^2 f_4 - f_3^2 + 2 f_1 f_2 f_3 - f_2^2)x^3 \end{aligned} \tag{A3}$$

$$Q(x) = (f_1 f_3 - f_2^2) + (f_2 f_3 - f_1 f_4)x + (f_2 f_4 - f_3^2)x^2 \tag{A4}$$

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Resumen. Se representan los desarrollos en serie de virial para la presión, correspondiente a las ecuaciones de estado para gases reales de Redlich-Kwong y Peng-Robinson, se representa por medio de aproximantes de Padé. Las representaciones de Padé se emplean subsecuentemente para determinar las funciones de separación reducidas de sistemas de componentes puros descritos por las ecuaciones de los dos modelos.