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Virial series expansions and gas-liquid transition predictions from two-parameter real gas models

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Abstract. The popular two-parameter cubic equations of state of the perturbation type proposed by Redlich and Kwong, and Peng and Robinson, and known to be capable of representing both vapor and liquid behavior, also possess virial coefficients to all orders. This last feature is exploited in the present study, whereby the series expansions in powers of density for both model equations of state are analyzed employing the Padé approximant procedure in an effort to predict the condensed phase branch. The behavior of the thermodynamic properties inherent to both these models in the near-critical region is also examined.

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1. Introduction

The van der Waals equation of state and the Ford model have been utilized by Aguilera-Navarro *et al.* [1] in an elegant study of whether virial series expansions for the pressure are useful in the determination of the point at which condensation occurs. Since the virial coefficients to all orders for both of the equations of state associated with these theories are known, the models in question are natural choices to consider in the inquiry of whether the equations of state, put in the form of virial series expansions, contain information relevant to the condensed phases.

In this report we propose to complement the work of Ref. [1] by including an examination of the two-parameter equations of state suggested by Redlich and Kwong, [2] and Peng and Robinson [3]. Although relatively simple algebraically, both of these equations describe not only imperfect gas behavior, but also condensation and regions of vapor and liquid metastability. Furthermore, they predict critical phenomena and also conform to the law of corresponding states; and, of course, they may be expressed in the form of a virial expansion. The computational ease of the Redlich-Kwong (RK) and Peng-Robinson (PR) equations, their reasonably high degree of accuracy, and the wide range of properties which can be treated recommend them highly; indeed these equations are among the most commonly employed in the calculation of the thermodynamic functions for pure materials [4,5]. The Redlich-Kwong and Peng-Robinson equations have been recently employed to predict the compressibility factors and the simple-fluid reduced departure functions of a gas from the ideal-gas state [6].

Following the procedure employed in Ref. [1], in both cases studied in this work we inquire whether the analytic continuation of the low-density expansion of the pressure into the twophase region exhibit the inherent behavior typical of the pressure-density isotherms in these model equations.

Condensation usually occurs at the equilibrium point. If the vapor undergoes maximum supersaturation then the spinodal is the condensation point. Since the Padé *extrapolant* technique [7] affords a convenient method for accurately representing a truncated virial series, the low-density expansions on the pressure obtained in the present work will be represented by Padé approximants, which will then be examined for the presence of a spinodal point, *i.e.*, a "physically reasonable" value of the density at which condensation occurs.

2. Formalism

As is well-known, besides the van der Waals expression there are several commonly encountered *two-parameter* equations of state for continuum fluids, each with its own adherents [8]. Among these we find the relations suggested by Berthelot [9], Dieterici [10], Redlich-Kwong, and Peng-Robinson. The Berthelot equation of state provides far more accurate spinodals than does the van der Waals equation of state [11]. The Dieterici equation of state has no liquid spinodals at negative pressures. In the present work, we have chosen to consider only the last two models listed.

To establish a link with the work reported in Ref. [1] and for a quick reference we begin by writing the van der Waals approximation to the equation of state of a real gas:

$$P = \frac{kT}{v-b} - \frac{a}{v^2} \equiv P_{\text{kin}} + P_{\text{coh}}, \tag{1}$$

where P is the total pressure within the fluid, T is the absolute temperature, k is Boltzmann's constant, and v the specific volume $v = V/N$, N being the total number of particles and V the volume of the container. The parameters a and b are both positive. As is well known, the first term in Eq. (1) is the kinetic, translational, or external pressure, whereas the second term is the configurational pressure, also known as the cohesive pressure. In Eq. (1), b is the minimum value of v for the liquid state. In terms of the number density $\rho = v^{-1}$, the van der Waals equation reads

$$\frac{P}{kT} = \frac{\rho}{1 - b\rho} - \frac{a\rho^2}{kT}. \tag{2}$$

The equation of state proposed by Redlich-Kwong, and the precursor of many modified forms, is [2]

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

while the relation suggested by Peng-Robinson is [3]

$$\frac{P}{kT} = \frac{\rho}{1 - b\rho} - \frac{a\rho^2}{kT(1 + 2b\rho - b^2\rho^2)}. \tag{4}$$

While in the original Peng-Robinson equation of state the parameter a depends on both the acentric factor and reduced temperature in a prescribed manner [3,5], in the present treatment [see Eq.(4)] a will be taken to be the value that the parameter attains in the original equation *at* the critical temperature [6].

The last three expressions above have the hard-sphere repulsion (kinetic) term in common; accordingly the quantity b has the same meaning in all three equations. Further in Eqs. (2), (3), and (4), a and b are phenomenological *positive* constants characteristic of the particular fluid, and are *different* for each semiempirical equation of state. Notice that the attractive pressure terms of both the RK and PR relations depend on the parameter b, a feature not shared by the van der Waals equation. In a recent paper Eberhart [12] has described six independent procedures of finding the parameters a and b from the three critical constants of a fluid. The choice of the method appears to have some impact on the values of the two parameters [12].

3.Model calculations

The critical isotherm has zero slope and zero curvature at the critical point. The mathematical statements of these conditions are

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0. \tag{5}$$

Performing the indicated differentiations on Eq. (3) leads to

$$\left.\begin{aligned} \rho_c &= \frac{\nu}{b}, \quad P_c = \frac{2\nu^3}{(1+\nu)^2(1-\nu)}\left(\frac{a}{kb}\right)^{2/3}\left(\frac{k}{b}\right) \\ T_c &= \left(\frac{1-\nu}{1+\nu}\right)^2\left(\frac{a}{kb}\right)^{2/3} \end{aligned}\right\} \qquad \text{(RK)} \qquad (6)$$

where the dimensionless quantity ν is the real solution of the cubic equation $\nu^3 + 3\nu^2 + 3\nu - 1 = 0$. A slight rearrangement of this equation yields $(\nu + 1)^3 = 2$, thus giving $\nu = 2^{1/3} - 1 = 0.259921$. Since it will be useful for overview and comparison purposes we will leave ν in the general form given by Eq. (6), that is $\nu = b\rho_c$. For the PR equation a similar treatment based upon the critical conditions, Eq. (5), gives the set of results:

$$\left.\begin{aligned} \rho_c &= \frac{\nu}{b}, \quad P_c = \frac{(\nu^3+3\nu^2-3\nu+3)\nu^3}{(1+2\nu-\nu^2)^3}\left(\frac{a}{b}\right) \\ T_c &= \frac{2\nu(\nu+1)(1-\nu)^2}{(1+2\nu-\nu^2)^2}\left(\frac{a}{kb}\right) \end{aligned}\right\} \qquad \text{(PR)} \qquad (7)$$

where ν is the real solution of the equation $3\nu^3 + 3\nu^2 + 3\nu - 1 = 0$, namely, $\nu = 0.253076$.

Introducing the reduced state variables

$$\pi \equiv \frac{P}{P_c}, \qquad y \equiv \frac{\rho}{\rho_c}, \qquad t \equiv \frac{T}{T_c}, \qquad (8)$$

equation (3) develops into the following expression in a self-explanatory notation

$$\pi_{\mathrm{RK}}(y) = \frac{1}{Z_{\mathrm{RK}}}\frac{yt}{(1-\nu y)} - \frac{(1+\nu)^3 y^2}{2\nu t^{1/2}(1+\nu y)}, \qquad (9)$$

in which Z_{RK}, the compressibility factor of a Redlich-Kwong system at the critical point, is given by the expression $Z_{\mathrm{RK}} = 2\nu^2/(1-\nu)^3$. Numerically $Z_{\mathrm{RK}} = 1/3$.

Using the new dimensionless variables it is an easy algebraic task to establish that the PR equation of state, Eq. (4) in reduced units, takes the form

$$\pi_{\mathrm{PR}}(y) = \frac{1}{Z_{\mathrm{PR}}}\frac{yt}{(1-\nu y)} - \frac{(\nu^2-2\nu-1)^3 y^2}{\nu(\nu^3+3\nu^2-3\nu+3)(\nu^2 y^2-2\nu y-1)}, \qquad (10)$$

where

$$Z_{\text{PR}} = \frac{\nu^2(\nu^3 + 3\nu^2 - 3\nu + 3)}{(2\nu^3 + 3\nu^2 + 1)(1-\nu)^3}.$$

In this case, numerically, $Z_{\text{PR}} = 0.307399$.

For the sake of comparison the van der Waals equation of state in reduced form is presented here,

$$\pi_{\text{vdW}}(y) = \frac{1}{Z_{\text{vdW}}} \frac{yt}{(1-\nu y)} - \frac{y^2}{\nu}, \tag{11}$$

where $Z_{\text{vdW}} = \nu^2/(1-\nu)^3$, and $\nu = 1/3$, so that $Z_{\text{vdW}} = 3/8$.

We will now analyze possible divergences of the pressure expressed as a power series in the density by representing the series by a Padé extrapolant. The reasons for this are twofold: first, the Padé approximant possesses zeroes, just as the truncated series that it represents, but also has *poles* and it is thus capable of describing singularities; second, being an *extrapolant*, the Padé approximant representation will be valid further away from the radius of convergence of the original truncated virial series that it represents [7].

Expanding Eq. (9) about zero reduced density as an infinite virial series and then extrapolating the $y = 0$ expansion to finite (physical) y by means of a Padé approximant gives [6]

$$\pi_{\text{RK}}(y) = \frac{ty}{Z_{\text{RK}}} \left[1 + \sum_{n=1}^{\infty} B_{n+1}^{\text{RK}}(t) y^n \right] \mathrel{\widehat{=}} \frac{ty}{Z_{\text{RK}}} [L/M](y), \tag{12}$$

with

$$B_{n+1}^{\text{RK}}(t) = \nu^n [1 + \beta_n^{\text{RK}}(t)], \qquad n = 1, 2, 3, \ldots$$

where

$$\beta_n^{\text{RK}}(t) = \frac{(-1)^n}{3\nu^2 t^{3/2}}.$$

The symbol $\widehat{=}$ in Eq. (12) means "represented by". The quantities $B^{\text{RK}}(t)$ are the reduced virial coefficients of the RK equation of state. Since $\nu (= 0.26) < 1$, $\nu^n \ll 1$, it can be readily seen that the higher the order of the reduced virial coefficient, the smaller its contribution to the power-series expansion. Furthermore, *all* the virial coefficients are temperature-dependent; this feature contrasts markedly with the virial coefficients due to a van der Waals system, where *only* the second (reduced) virial coefficient depends on the temperature [1,13].

The reduced virial expansion for a pure PR system is given by [6]

$$\pi_{\mathrm{PR}}(y) = \frac{ty}{Z_{\mathrm{PR}}}\left[1 + \sum_{n=1}^{\infty} B_{n+1}^{\mathrm{PR}}(t) y^{n}\right] \mathrel{\widehat{=}} \frac{ty}{Z_{\mathrm{PR}}}[L/M](y), \tag{13}$$

with

$$B_{n+1}^{\mathrm{RP}}(t) = \nu^{n}[1 + \beta_{n}^{\mathrm{PR}}(t)], \qquad n = 1, 2, 3, \ldots$$

where

$$\beta_{n}^{\mathrm{PR}}(t) = \frac{D_n (1 + 2\nu - \nu^2)^3}{(2\nu^3 + 3\nu^2 + 1)(1 - \nu)^3 t}.$$

In Eq. (13), $\nu = 0.253076$. The D_n's appearing in the last expression above are the coefficients in the Maclaurin expansion of the function $f(u) = (u^2 - 2u - 1)^{-1}$. The first seven values of D_n are: -1, 2 ,-5, 12, -29, 70 and -169. For an arbitrary (yet subcritical) value of the reduced temperature, and for n greater than 3, the absolute value of each reduced virial coefficient is $(1 + \sqrt{2})\nu$ times the preceding one.

Tables I and II list p_i (numerator) and q_i (denominator) coefficients for some selected Padé approximants corresponding to a reduced temperature $t = 0.5$ for the infinite series virial expansions (12) and (13) of the Redlich-Kwong, and Peng-Robinson equations of state, respectively. A careful numerical study reveals that at the temperatures considered in this work, namely, $t = 0.5$ and $t = 0.75$, the Padé approximant reproduces the exact RK curve including, of course, the poles which, translated into the variable x, are located at $x = -0.259921$ and 0.259921. The first of these poles is, clearly, physically unrealistic. The second pole corresponds to the reduced *hard-sphere* volume. Expressed in terms of the reduced volume x, the polar singularities of the PR equation occur at $x = -0.610980$, 0.104828, and 0.253076. Again, the first pole is nonphysical; the second one is much lower than the limit below which the scaled volume cannot be further reduced. The third pole corresponds to the scaled hard sphere volume. The poles are correctly reproduced by the [2/3] approximant. The [2/3] Padé approximant also reproduces the exact behavior of the pressure in the coexistence region exhibited by the PR equation.

The spinodal points y_s are found from the requirement that

$$\left(\frac{\partial \pi}{\partial y}\right)_{t,N} = 0. \tag{14}$$

In taking the partial derivative (14) the system is constrained to be isothermal and of constant mass. The equation that must be solved to obtain the values of y_s for a pure Redlich-Kwong fluid is Eq. (14), which through the use of Eq. (10) develops

$[L/M]$	[2/1]	[2/2]	[3/1]	[3/2]	[4/0]
p_1	−3.142208	−3.367369	−3.067323	−3.367369	−3.367369
p_2	0.252166	0.942809	–	0.942809	1.010368
p_3	–	–	0.075662	–	−0.227496
p_4	–	–	–	–	0.068259
q_1	0.225161	–	0.300047	–	–
q_2	–	−0.067559	–	−0.067559	–

TABLE I. Numerator (p_i) and denominator (q_i) polynomial coefficients of some selected Padé approximants based on the Redlich-Kwong virial expansion corresponding to the reduced subcritical temperature $t = 0.5$. Notice that the approximants $[2/2](y)$ and $[3/2](y)$ are equal.

$[L/M]$	[2/1]	[2/3]	[3/1]	[3/2]	[4/3]
p_1	−2.125214	−2.468689	−2.099488	−2.504954	−2.468689
p_2	−0.053900	0.688815	−0.123920	0.737782	0.688815
p_3	–	–	0.040384	0.062238	–
p_4	–	–	–	–	–
q_1	0.596551	0.253076	0.622277	0.216811	0.253076
q_2	–	−0.192143	–	−0.241881	−0.192143
q_2	–	0.016209	–	–	0.016209

TABLE II. Numerator (p_i) and denominator (q_i) polynomial coefficients of some selected Padé approximants based on the Peng-Robinson virial expansion corresponding to the reduced subcritical temperature $t = 0.5$. Notice that the approximants $[2/3](y)$ and $[4/3](y)$ are equal.

into

$$y_s^4 - \left(\frac{3+\phi}{\nu^2}\right) y_s^2 + \left(\frac{2(1-\phi)}{\nu^3}\right) y_s - \frac{\phi}{\nu^4} = 0, \qquad \text{(RK)} \tag{15}$$

where ϕ is a function that depends on the reduced temperature t according to the expression

$$\phi(t) = \frac{(1-\nu)^3}{2} t^{3/2}$$

with $\nu = 0.259921$. The corresponding equation for a pure component system described by the Peng-Robinson relation (10) is

$$y_s^4 + \left[\frac{2(\psi-2)}{(1-2\psi)\nu}\right] y_s^3 + \left[\frac{2(1+\psi)}{(1-2\psi)\nu^2}\right] y_s^2 + \left[\frac{2(2-\psi)}{(1-2\psi)\nu^3}\right] y_s + \frac{1}{\nu^4(1-2\psi)} = 0 \qquad \text{(PR)} \tag{16}$$

where

$$\psi(t) = \frac{(1 + 2\nu - \nu^2)^3}{(2\nu^3 + 3\nu^2 + 1)(1 - \nu)^3 t}$$

with $\nu = 0.253076$. For a particular value of the reduced temperature the spinodal equations (15) and (16) were solved employing a root finder algorithm. Since it will be needed in the treatment, we denote by $y_-(= 1/x_+)$ and $y_+(= 1/x_-)$ the values of the reduced density which define the stability limits.

At fixed mass and reduced temperature, term by term differentiation with respect to y of the virial expansions (12) and (13) yields

$$\begin{aligned} 0 = \frac{\partial \pi(y)}{\partial y} &= \frac{ty}{Z}\left[1 + \sum_{n=1}^{\infty}(n+1)B^{*}_{n+1}(t)y^n\right] \\ &\mathrel{\widehat{=}} \frac{ty}{Z}[N/0](y). \end{aligned} \tag{17}$$

For an arbitrary subcritical isotherm Eq. (17) has two positive zeroes which define the spinodal points. In Fig. 1 we have plotted the estimates of the spinodal points y_- and y_+ versus the reciprocal of the number of terms at which Eq. (17) is truncated. From Fig. 1 it is observed that Eq. (17) predicts for the Redlich-Kwong equation spinodal points for different temperatures tending to the exact values obtained *directly* from the equation of state. In call cases studied it is found that the estimates for y_+ from the successive $[N/0]$ approximants approach rapidly a linear behavior with respect to $1/N$, and in fact the plot becomes nearly flat for values of N greater than 6.

For a pure material described by the Peng-Robinson equation we observe that while the exact value y_- is predicted to five figures by the Padé $[10/0](y)$, to obtain the correct value of y_+ higher order approximants are necessary. For example, at $t = 0.75$ the exact values of the spinodal points calculated from Eq. (16) are: $y_- = 0.405090$, and $y_+ = 1.907606$. Taking $N = 14$ we obtain from Eq. (17) $y_- = 0.405093$ and $y_+ = 1.284148$, showing that the convergence of the estimates of the Padé approximants $[N/0]$ to the exact value of y_+ is rather low.

4. Behavior of the thermodynamic properties in the near-critical region

Several interesting side issues to the main theme of the present work will now be considered. Assuming the validity of the Redlich-Kwong equation of state for a pure material at a reduced temperature t slightly below the critical temperature, we might ask what is the density ratio of liquid to gas in the near-critical region. A long but straightforward procedure involving the Maxwell equal area construction [14] gives

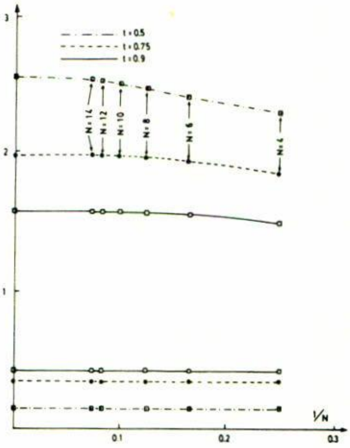

FIGURE 1. Spinodal values y_+, and y_- for different temperatures for the Redlich-Kwong relation as solution of the exact Eq. (9) and of $[N/0](y)$ Eq. (17), obtained for different values of N. In all cases considered a polynomial with $N = 6$ reproduces with five figure accuracy the value at which the smaller spinodal point y_- occurs.

to *lowest* order in $(1-t)^{1/2}$

$$\frac{\rho_{\rm L}}{\rho_{\rm G}} \cong 1 + 6.5(1-t)^{1/2}. \qquad \text{(RK)} \tag{18}$$

Note that this ratio falls with rising temperature, and yields at the critical point $\rho_{\rm L} = \rho_{\rm G}$, as expected from classical considerations. The exponent of $(1-t)$ in Eq. (18) is, however, in disagreement with the value experimentally observed on real systems [15,16]. The van der Waals equation predicts a result similar to the one given by Eq. (18), namely

$$\frac{\rho_{\rm L}}{\rho_{\rm G}} \cong 1 + 4(1-t)^{1/2}. \qquad \text{(vdW)} \tag{19}$$

Another interesting and important question along the same lines is: How does the isothermal compressibility K_T approach its critical value, *i.e.*, what is the behavior of K_T as $t \to 1$ along the critical isochore? To find the compressibility

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{20}$$

for a Redlich-Kwong system, we first expand the reduced pressure given by Eq. (10) about the critical point in powers of the dimensionless parameters ϵ and θ defined as

$$\epsilon \equiv (1-t); \qquad \theta \equiv y^{-1} - 1. \tag{21}$$

The result of such expansion is

$$\pi_{\mathrm{RK}} = 1 - 5.6\epsilon + 8.2\epsilon\theta - 1.07\theta^3 \tag{22}$$

which predicts that in the vicinity of the critical point the critical isotherm ($\epsilon = 0$) is a cubic curve, and the coexistence curve a parabola. Again, for the sake of comparison the expansion of the reduced van der Waals equation in terms of the small variables ϵ, and θ is presented here [17]:

$$\pi_{\mathrm{vdW}} = 1 - 4\epsilon + 6\epsilon\theta - 1.5\theta^3. \tag{23}$$

The reduced isothermal compressibility in the vicinity of the critical point is readly shown to be

$$K_T^* = -\left[(1+\theta)\left(\frac{\partial\pi}{\partial\theta}\right)_\epsilon\right]_{\theta=0}^{-1} \propto \epsilon^{-1}. \qquad \begin{pmatrix}\mathrm{vdW}\\ \mathrm{RK}\end{pmatrix} \tag{24}$$

We thus see that in both, the van der Waals and Redlich-Kwong equations, very close to but below T_c, the static isothermal compressibility diverges to infinity as the reciprocal of the temperature difference from critical, $(T - T_c)^{-1}$. The exponent of ϵ in Eq.(24) is in disagreement with the value determined from experiments [15,16].

By a standard procedure it can be demonstrated that on the *coexistence curve*

$$P - P_c = 5.6P_c[-\epsilon + 6.5\epsilon^2 + \mathcal{O}(\epsilon^3)], \qquad (\mathrm{RK}) \tag{25}$$

where ϵ is small and positive and P_c is given by Eq. (6) with $\nu = 0.259921$. On the critical isochore ($\theta = 0$), and in the vicinity of the critical point in follows from Eq. (22) that $P - P_c$ is proportional to ϵ. Indeed

$$P - P_c = -5.6P_c\epsilon. \qquad (\mathrm{RK}) \tag{26}$$

From Eqs. (25) and (26) it can be readily seen that for a pure Redlich-Kwong fluid the second partial derivative of the pressure with respect to temperature is *finite* at the critical point but has a jump discontinuity in going from the critical isochore to the existence curve.

The van der Waals results corresponding to Eqs. (25) and (26) are [18]

$$P - P_c = 4P_c[-\epsilon + 1.2\epsilon^2 + \mathcal{O}(\epsilon^3)], \qquad (\mathrm{vdW}) \tag{27}$$

a result which, we reiterate, is valid only on the coexistence curve, and

$$P - P_c = -4P_c\epsilon, \qquad (\mathrm{vdW}) \tag{28}$$

an expression valid on the critical isochore. In Eqs. (27) and (28) the temperature parameter ϵ is small and positive, and P_c is the critical pressure of a van der Waals fluid, *i.e.*, $P_c = a/27b^2$.

For very small values of the parameters ϵ and θ the results of our calculations show that

$$\theta = 3.27\epsilon^{1/2}. \qquad \text{(RK)} \tag{29}$$

Hence, the volume parameter θ vanishes at the critical temperature, as expected [17]. For comparison, the corresponding result for the van der Waals (mean-field) model is [17]

$$\theta = 2\epsilon^{1/2}. \qquad \text{(vdW)} \tag{30}$$

The similarities between the predictions of the Redlich-Kwong, and the van der Waals equations of state for the density ratio, isothermal compressibility, and jump discontinuities in $(\partial^2 P/\partial T^2)_V$ in the near-critical region are not fortuitous [15,16]. Indeed, as has been pointed out elsewhere [17], equations such as the ones treated in the present work are reliable approximations "only when the range of the attractive potential is large compared to the scale of the relevant correlations". We thus do not feel it practical or necessary to develop equations such as (18), (22), (24), (25) and (26) for the Peng-Robinson equation of state, as the new relations would exhibit near the critical point a behavior *similar* to the one predicted by the van der Waals and Redlich-Kwong equations.

5. Concluding remarks

In this article an attempt has been made to construct improved equations of state capable of describing not only imperfect gas behavior, but also condensation and regions of vapor and liquid metastability. The way by which various derivative quantities approach their critical value has been also examined in this work.

The Padé representations to the *low-density expansions* of the reduced pressure for the Redlich-Kwong and Peng-Robinson two-parameter model equations examined here have been found to reproduce in the coexistence region the oscillatory behavior typical of the isotherms in both of these models. This feature of the method could be valuable to gain some insight into the gas-liquid phase transition predicted by *realistic* equations of state.

Clearly, if no restrictions are placed on the number of parameters employed nor on the complexity of the relation, it is possible to develop highly accurate empirical of semiempirical equations of state to describe thermodynamic properties of substances over a wide range of conditions. An amenable, yet realistic, equation of state that could be treated with the method employed in this article is the one proposed in 1986 by Kim, Lin, and Chao [4]. These authors represent the repulsive part of the pressure by an approximation of the Carnahan and Starling [12,19] pressure equation of state for hard-sphere fluids, known to be in excellent agreement with computer simulations.

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15. J.L. Lebowitz, and E.M. Waisman in *The Liquid State of Matter: Fluids, Simple and Complex*, North-Holland, New York (1982), E.W. Montroll and J.L. Lebowitz, eds.
16. There is a critical region close to the critical point where the analytical equations of state for pure fluids fail. Three excellent papers dealing mainly with experimental aspects of critical phenomena are: A. Levelt Sengers, R. Hocken, and J.V. Sengers, *Physics Today* **30** (12) (1977) 42; S.C. Greer and M.R. Moldover, *Ann. Rev. Phys. Chem.* **32** (1981) 233; A. Kumar, H.R. Krishnamur and E.S.R. Gopal, *Phys. Rep. (Netherlands)* **98** (1983) 57.

17. D.L. Goodstein, *States of Matter*, Prentice-Hall, Englewood Cliffs, NJ (1975), chapter 6.
18. R.J. Baxter, *Exactly Solved Models in Statistical Mechanics*, Academic Press, New York (1982).
19. N.F. Carnahan and K.E. Starling, *J. Chem. Phys.* **51** (1969) 635.

Resumen. Las ecuaciones cúbicas de estado de dos parámetros del tipo perturbativo de Redlich-Kwong y Peng-Robinson, útiles en la descripción del comportamiento gaseoso y líquido, comparten la propiedad de poseer coeficientes de virial en todos los órdenes. Esta última característica se aprovecha en el presente trabajo; los aludidos desarrollos en serie de potencias en la densidad de ambas ecuaciones de estado se analizan mediante la técnica de los aproximantes de Padé, en un esfuerzo por predecir la fase condensada. El comportamiento de las propiedades termodinámicas inherentes a ambos modelos en la proximidad de la región crítica recibe un tratamiento especial.