International Journal of Thermophysics, Vol. 10, No. 1, 1989

New Methods for Locating Phase Boundaries[1]

G. Fescos,[2] J. M. Kincaid,[2] and G. Morrison[3]

A new geometric representation for the dew/bubble conditions of a special class of polydisperse fluids is used to develop series expansion representations for the location of the top of the dew/bubble and shadow curves and for an expansion around the top of the dew/bubble and shadow curves. An excellent approximation for the one-comonent van der Waals coexistence is given as a special illustration of the method.

KEY WORDS: coexistence curve; critical point; dew/bubble curve; phase transitions; polydisperse.

1. INTRODUCTION

In a recent study of a special class of polydisperse fluids we found a particularly simple geometric representation of the dew/bubble conditions [1]. In that representation the problem of locating the dew/bubble and shadow curves is reduced to locating the points of intersection of two curves. Once these points of intersection are located, the composition of the nucleating phase is easily determined. In this paper we show that it is possible to obtain explicit solutions of the dew/bubble conditions in the form of power series expansions. By forming Padé approximants from these series it is possible to create compact expressions for the phase boundaries that provide very accurate representations over a wide range of temperatures and densities. Although the models on which we demonstrate our techni-

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Mechanical Engineering, SUNY at Stony Brook, Stony Brook, New York 11794, U.S.A.

[3] Thermophysics Division, National Institute of Standards and Technology (formerly National Bureau of Standards), Gaithersburg, Maryland 20899, U.S.A.

0195-928X/89/0100-0075$06.00/0

que are rather simple, it seems likely that the method may be applied to more complicated models.

We begin in Section 2 by describing our method for the simple case of the one-component van der Waals model. In Section 3 we define two models for polydisperse fluids for which we exhibit explicit solutions and express the dew/bubble conditions in a form appropriate for our calculations. Section 4 contains a description of our series expansion method for locating the top of the dew/bubble and shadow curves and for an expansion around the top of the dew/bubble curve.

2. THE ONE-COMPONENT VAN DER WAALS MODEL

The van der Waals model provides one of the simplest models of a fluid that exhibits the qualitative features of most real fluids. Although the coexistence curve of the van der Waals model is discussed in almost every textbook on thermodynamics, no closed-form expression has been found to represent its coexistence curve. In this section we come very close to providing such an expression.

Let us begin by stating the relevant equations for the pressure, p, and chemical potential, μ, of the model:

$$p(T, \rho) = \frac{8T\rho}{(3-\rho)} - 3\rho^2 \tag{1}$$

and

$$\mu(T, \rho) = \left[\ln\left[\frac{\rho}{(3-\rho)}\right] + \frac{\rho}{(3-\rho)}\right] - \frac{9}{4}\rho \tag{2}$$

Here ρ is the number density and T is the temperature. [We have used dimensionless variables: energies are reduced by $8a/(27b)$, volumes by $3b$, and pressures by $a/(27b^2)$, where a and b are the van der Waals constants.] Two phases with densities denoted by x and y, respectively, coexist in equilibrium if

$$p(T, x) = p(T, y) \qquad \text{and} \qquad \mu(T, x) = \mu(T, y) \tag{3}$$

For $T > 1$ the only solution of these equations is the trivial solution $x = y$ —there is only one phase. When $T < 1$, the nontrivial solutions of these two equations, $x(T)$ and $y(T)$, define the coexistence curve. In addition to the usual geometric representations for the equilibrium conditions [e.g., the equal area rule, the bitangent construction, or the minimization of $\mu(T, p)$], we find it useful (especially in the case of the polydisperse fluid models considered later) to define two new functions whose zeros are the roots of Eqs. (3). Let

$$f(T, x, y) = p(T, x) - p(T, y) \tag{4}$$

and

$$g(T, x, y) = \exp\left[\frac{\mu(T, x) - \mu(T, y)}{T}\right] - 1 \tag{5}$$

Clearly Eqs. (3) are satisfied if $f(T, x, y) = g(T, x, y) = 0$. Figure 1 shows the curves defined by $f = 0$ and $g = 0$ for several values of T. The curve $f = 0$ is especially simple. After factoring out the trivial solution it reduces to $0 = (8T - 9x + 3x^2) + (6x - x^2 - 9)\,y + (3 - x)\,y^2$. It is a simple matter to show that for $x \in (0, 3)$ this equation has no real roots if $T > 1$ and two real roots if $T < 1$; the curve is symmetric about the line of trivial solutions $x = y$; it is perpendicular to that line at the spinodal points (i.e., points for which $\partial p/\partial \rho = 0$). At the critical temperature, $T_c = 1$, the two real roots become identical: $x = y = 1$. Thus as $T \to 1$ from below the curve, $f = 0$ shrinks to a point.

The curve defined by $g = 0$ is also symmetric about the line of trivial

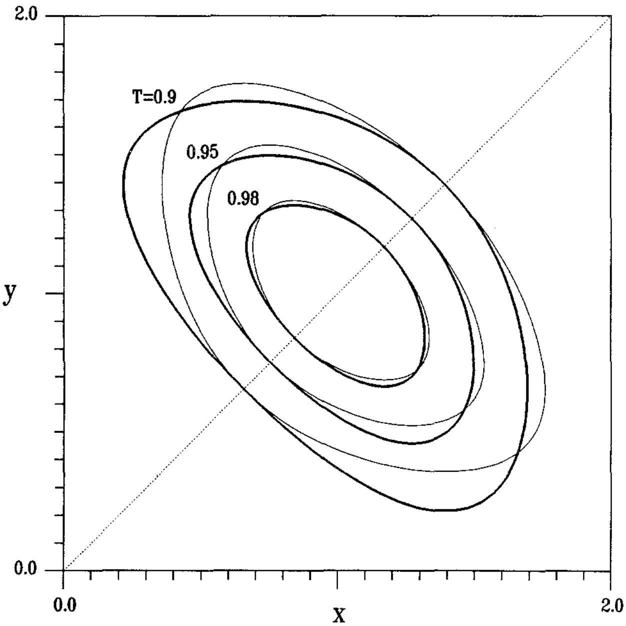

Fig. 1. The f and g curves (—— and ——, respectively) for the one-component van der Waals model in the density–density plane for $T = 0.9$, 0.95, and 0.98.

Table I. Series Expansion and Padé Coefficients for the One-Component van der Waals Model

i	Y_i	T_i	p_i	q_i
0			0	1.0
1	−1	0	0	1.802090100442137
2	1/5	−1/4	0.25d0	0.4406982057132636
3	−1/25	1/20	0.4005225251105341	−0.5865855584276499
4	19/350	−9/200	0.06507004640620901	−0.1693140856083776
5	−257/8750	193/7000	−0.1151586739441081	0.0636907910635397
6	82/3125	−1537/70000	−0.02089687985009113	0.006714940882240352
7	−30473/1531250	6009/350000	0.008241551164959003	−0.001514001036457516
8	5682007/336875000	−174131/12250000		0.0001500352791753875
9	−4788983/336875000	4039291/336875000		
10	9416877049/766390625000	−139209837/13475000000		
11	−41304330271/3831953125000	55422640939/6131125000000		
12	365903790401/38319531250000	−22317626143/2786875000000		
13	−205052895637/23949707031250	1099077458301/153278125000000		
14	352502341882081/45600242187500000	−69486569467703/10729468750000000		
15		10775040909775247/18240096875000000		

solutions; it is perpendicular to that line at the spinodal points. The equation $g=0$ is transcendental so it is difficult to classify the solutions analytically, however, we find that it always consists of a closed loop. (The f and g curves are always closed loops in the x–y plane when $T<1$.)

The solution of the equilibrium conditions is represented by the points of intersection of the f and g curves (excluding the intersections with the line of trivial solutions). The coexistence curve can be obtained in the form of a series expansion by setting $T=1+\Delta T$, $x=1+\Delta x$, and $y=1+\Delta y$, expanding f and g about $\Delta x=\Delta y=\Delta T=0$, dividing out the trivial solution $\Delta x=\Delta y$, setting $\Delta T=\sum_{i=1}^{\infty} T_i \Delta x^i$ and $\Delta y=\sum_{i=1}^{\infty} Y_i \Delta x^i$, and solving for the coefficients $\{T_i\}$ and $\{Y_i\}$. We have determined these coefficients up to T_{15} and Y_{14}; they are given in Table I.

In Fig. 2 we compare the coexistence curve of this model obtained by numerical solution to that obtained from the series solution. In addition, we show the [7/8] Padé approximant

$$T_{\text{Padé}}=1-\left(\sum_{i=0}^{7} p_i \Delta x^i\right)\Bigg/\left(1+\sum_{i=0}^{8} q_i \Delta x^i\right) \tag{6}$$

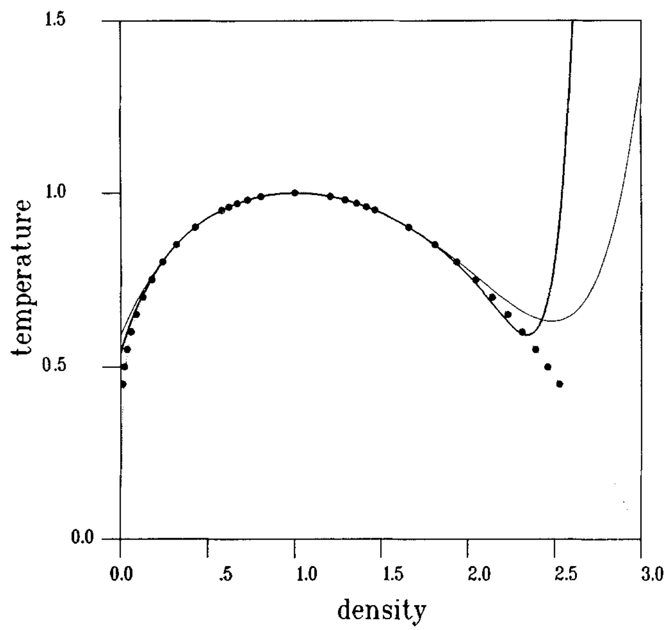

Fig. 2. The coexistence curve of the one-component van der Waals model in the density–temperature plane. The filled circles are points calculated numerically; the thin and thick lines are the 7- and 13-term series representations of the coexistence curve; the dashed line is the [7/8] Padé of the 13-term series.

of the series for $T(x)$. The approximant has been constructed so that it gives the correct solution at $T=0$. The series expansions are fairly accurate for temperatures above 0.6. Equation (6) is quite accurate over the entire interval [0, 1].

3. TWO SIMPLE POLYDISPERSE FLUID MODELS

The two models analyzed in this section are specific members of a special class of models whose equilibrium conditions may be solved by simple numerical methods [1]. The two models are special cases of a polydisperse van der Waals model, and each has the feature that p depends on the mole fraction distribution density, $F(I)$, only through its first moment and $\mu(I)$, aside from the ideal mixing terms, is a linear function of

Table II. Functions Defining Models A and B

Model A

$$a(I, J) = (I+J)/2, \quad b(I) = 1$$

$$p(T, \rho \mid F) = 8T\rho/(3-\rho) - 3\rho^2 z$$

$$\mu(I, T, \rho \mid F) = T\left[\ln F(I) + \ln\left(\frac{\rho}{3-\rho}\right) + \frac{\rho}{3-\rho}\right] - \frac{9}{8}\rho(z+I)$$

$$C_1 = \ln\left(\frac{x}{3-x}\right) + \frac{x}{3-x} - \frac{9x}{8T} - \ln\left(\frac{y}{3-y}\right) - \frac{y}{3-y} + \frac{9yz_y}{8T}$$

$$C_2 = 9(y-x)/(8T)$$

Model B

$$a(I, J) = 1, \quad b(I) = b_0 + b_1 I$$

$$p(T, \rho \mid F) = 8T\rho/[3-\rho(b_0+b_1 z)] - 3\rho^2$$

$$\mu(I, \rho \mid F) = T\left\{\ln F(I) + \ln\left[\frac{\rho}{3-\rho(b_0+b_1 z)}\right] + \frac{\rho(b_0+b_1 I)}{3-\rho(b_0+b_1 z)}\right\} - 9\rho/4$$

$$C_1 = \ln\left(\frac{x}{3-x}\right) + \frac{xb_0}{3-x} - \frac{9x}{4T} - \ln\left[\frac{y}{3-y(b_0+b_1 z_y)}\right] - \frac{yb_0}{3-y(b_0+b_1 z_y)} + \frac{9y}{4T}$$

$$C_2 = \frac{xb_1}{3-x} - \frac{yb_1}{3-y(b_0+b_1 z_y)}$$

I and depends only on the first moment of F. Here I is a continuous species label. The equations defining the pressure and chemical potentials of each of these models are given in Table II. (The same set of dimensionless variables employed in Section 2 is used here.) Model A is a polydisperse van der Waals model for which the mean attractive potential energy parameter, $a(I, J)$, is given by $(I+J)/2$ and the excluded volume parameter, $b(I)$, is constant. In model B, $a(I, J)$ is constant and $b(I)=b_0+b_1 I$, with $b_0+b_1=1$. For each model we assume that $F(I)$ is a Schulz distribution with a mean value of 1 and a variance of $\varepsilon=1/v$: $F(I)=v^v I^{v-1} e^{-vI}/\Gamma(v)$, where Γ is the gamma function. The pressure and chemical potential depend on the first moment of F, which we denote by z.

At a dew/bubble point a bulk phase with density x and composition $F(I)$ is in equilibrium with a nucleating phase with density y and composition $F_y(I)$. For these models the dew/bubble conditions can be reduced to the following equations:

$$p(T, x)=p(T, y, z_y) \tag{7}$$

$$1=\exp(C_1)\left[\frac{v}{v-C_2}\right]^v \tag{8}$$

and

$$z_y=\frac{v}{v-C_2} \tag{9}$$

where z_y is the first moment of $F_y(I)=F(I)\exp(C_1+C_2 I)$, and the functions C_1 and C_2 are given in Table II.

For each model it is possible to solve Eq. (9) for z_y and use that expression to eliminate z_y from Eqs. (7) and (8). Thus, for a given T and ε, the dew/bubble conditions reduce to solving two equations [(7) and (8)] in two unknowns (x and y). As in the one-component case we introduce the functions f and g, which in this case we define to be

$$f(T, x, y, \varepsilon)=p(T, x)-p(T, y, z_y) \tag{10}$$

and

$$g(T, x, y, \varepsilon)=\varepsilon C_1-\ln(1-\varepsilon C_2) \tag{11}$$

The dew/bubble conditions are simply

$$f(T, x, y, \varepsilon)=0 \qquad \text{and} \qquad g(T, x, y, \varepsilon)=0 \tag{12}$$

For fixed T and ε the curves defined by Eqs. (12) have many of the same

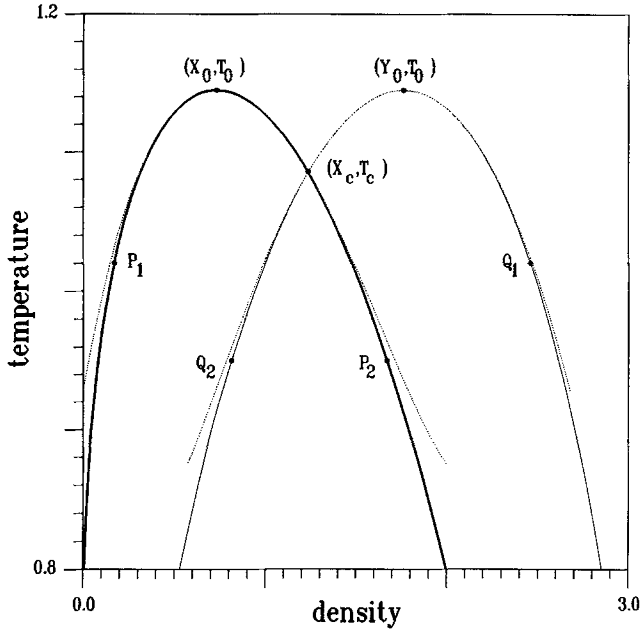

Fig. 3. The dew/bubble (——) and shadow (——) curves for model A in the density–temperature plane for $\varepsilon = 1/5$. (P_1, Q_1) and (P_2, Q_2) are examples of two coexisting phases. The critical point is at (X_c, T_c); the tops of the dew/bubble and shadow curves are denoted by (X_0, T_0) and (Y_0, T_0), respectively. The dotted curve represents the five-term series approximation.

features possessed by those of the one-component van der Waals model [1]. The dew/bubble curve, $x(T)$, and the shadow curve, $y(T)$, for model A with $\varepsilon = 1/5$ are shown in Fig. 3. Those curves were obtained by solving the equations $f = 0$ and $g = 0$ numerically.

4. SERIES EXPANSION METHOD

The method used to determine these curves by series expansion consists of several steps, each of which is described in the following subsections.

4.1. Locating the Tops of the Dew–Bubble and Shadow Curves

At the top of the dew/bubble and shadow curves, $dT/dx = dT/dy = 0$. On these curves, if we take T as a function of x and y as a function of x, the requirement that $dT/dx = dT/dy = 0$ leads to an additional equation:

$$h(T, x, y, \varepsilon) = \partial f/\partial x \times \partial g/\partial y - \partial f/\partial y \times \partial g/\partial x = 0 \tag{13}$$

Thus T_0, X_0, and Y_0 are the roots of Eqs. (12) and (13). To find these roots we begin by dividing out the trivial solution, $x=y$. To extract this trivial root the substitution $(T, x, y, \varepsilon)=(T_c+\delta T, X_c+\delta x, Y_c+\delta y, \varepsilon)$ is made in each equation. If the resulting equation is transcendental, the equation can be converted into a polynomial by expanding the equation about the point $(\delta x, \delta y, \delta T, \varepsilon)=(0, 0, 0, 0)$ in the form of a Taylor series and then dividing the root $(\delta x-\delta y)$ out. The transformed equations are denoted $\tilde{f}(\delta x, \delta y, \delta T, \varepsilon)=0$, $\tilde{g}(\delta x, \delta y, \delta T, \varepsilon)=0$, and $\tilde{h}(\delta x, \delta y, \delta T, \varepsilon)=0$. These equations can be rewritten in terms of x, y, and T by substituting $(\delta x, \delta y, \delta T)=(x-X_c, y-Y_c, T-T_c)$ into the $\tilde{f}$, $\tilde{g}$, and $\tilde{h}$ equations.

To calculate $X_0(\varepsilon)$, $Y_0(\varepsilon)$, and $T_0(\varepsilon)$ or, more precisely, $X_c+\delta x_0(\varepsilon)$, $Y_c+\delta y_0(\varepsilon)$, and $T_c+\delta T_0(\varepsilon)$, we assume that $\delta x_0(\varepsilon)$, $\delta y_0(\varepsilon)$, and $\delta T_0(\varepsilon)$ are analytic functions of ε and set $\delta x_0(\varepsilon)=\sum_{i=1}^{\infty} A_i\varepsilon^i$, $\delta y=\sum_{i=1}^{\infty} B_i\varepsilon^i$, and $\delta T=\sum_{i=1}^{\infty} C_i\varepsilon^i$. Substituting these series into $\tilde{f}$, $\tilde{g}$, and $\tilde{h}$ and expanding the results about $\varepsilon=0$ in the form of a Taylor series and then setting the coefficients of each power of ε in each of the resulting equations to zero yield a set of linear equations which can be solved for the A_i, B_i, and C_i's. These coefficients are listed in Tables III and IV.

Table III. Model A Series Coefficients for X_0, Y_0, and T_0

$A_1 = -9/9$
$A_2 = -513/640$
$A_3 = -61479/51200$
$A_4 = -6860619/5734400$
$A_5 = -1129535199/573440000$
$A_6 = -56134282311/26214400000$
$A_7 = -193394185731333/51380224000000$

$B_1 = 27/8$
$B_2 = 1431/640$
$B_3 = -31347/51200$
$B_4 = 1642437/5734400$
$B_5 = -314317827/573440000$
$B_6 = 25652716119/183500800000$
$B_7 = -41264995428729/5138022400000$

$C_1 = 9/16$
$C_2 = 81/128$
$C_3 = 3159/5120$
$C_4 = 1471851/1638400$
$C_5 = 228185019/229376000$
$C_6 = 14324480397/9175040000$
$C_7 = 2812799764539/1468006400000$
$C_8 = 10365224826624057/3288334336000000$

Table IV. Model B Series Coefficients for X_0, Y_0, and T_0

$A_1 = -b_1^2/2$
$A_2 = -(63b_1^4 - 20b_1^3)/40$
$A_3 = -(3157b_1^6 - 1580b_1^5)/400$
$A_4 = -(1028933b_1^8 - 693588b_1^7 + 65520b_1^6)/22400$
$A_5 = -(326333973b_1^{10} - 278335000b_1^9 + 51937200b_1^8 - 945000b_1^7)/1120000$

$B_1 = 5b_1^2/2$
$B_2 = (381b_1^4 - 40b_1^3)/40$
$B_3 = (9712b_1^6 - 2705b_1^5)/200$
$B_4 = (63853315b_1^8 - 2921856b_1^7 + 168840b_1^6)/22400$
$B_5 = (2035472421b_1^{10} - 1300347200b_1^9 + 171662400b_1^8 - 1890000b_1^7)/1120000$

$C_1 = b_1^2/4$
$C_2 = 9b_1^4/16$
$C_3 = (313b_1^6 - 60b_1^5)/160$
$C_4 = (55441b_1^8 - 21480b_1^7 + 600b_1^6)/6400$
$C_5 = (198142223b_1^{10} - 11477340b_1^9 + 1140300b_1^8)/448000$
$C_6 = (222169203b_1^{12} - 1707790800b_1^{11} + 310077600b_1^{10} - 8666000b_1^9)/8960000$

4.2. The Dew–Bubble and Shadow Curves

Our objective is to use the method of series expansions to determine the dew–bubble and shadow curves. We begin by noting that these curves are expected to be analytic functions of x, y, and T in the neighborhood of X_0, Y_0, and T_0; thus we choose to represent the dew–bubble curve by $T = T_0 + \sum_{i=1}^{\infty} T_i \Delta x^i$ and the shadow curve by $y = Y_0 + \sum_{i=1}^{\infty} Y_i \Delta x^i$, where $\Delta x = x - X_0$. Since $dT/dx = 0$, we anticipate that the curves are parabolic in the neighborhood of (X_0, T_0) and (Y_0, T_0), and thus $T_1 = 0$. The set of coefficients $\{T_i\}$ and $\{Y_i\}$ is obtained by substituting the above series into the $\tilde{f}$ and $\tilde{g}$ equations and expanding each of the resulting equations in the form of a Taylor series about $\Delta x = 0$. The coefficients of the powers of Δx yield a set of linear equations which can be solved for the T_i and Y_i's. The results are given in Table V. In Fig. 3 we compare the series expansion representation to the numerical solution for Model A with $\varepsilon = 1/5$. The series expansion appears to be accurate down to temperatures of about 0.9. When a few more coefficients are calculated and the Padé approximant is formed from them, we expect to have a very accurate representation. The critical point, (X_c, T_c), is accurately located by these series. Expansions for X_c and T_c in powers of ε are easily obtained.

Table V. Models A and B Series Coefficients for the Dew/Bubble and Shadow Curves

Model A

$Y_1 = -1 - 9\varepsilon/10 + 81\varepsilon^2/40 + 179577\varepsilon^3/448000 + 1983609\varepsilon^4/2560000 + 19545219\varepsilon^5/102400000$
$Y_2 = 1/5 - 81\varepsilon/200 + 999\varepsilon^2/3500 + 1613277\varepsilon^3/4480000 - 476515953\varepsilon^4/716800000$
$Y_3 = -1/25 - 153\varepsilon/700 - 351\varepsilon^2/2240 + 238475421\varepsilon^3/358400000$
$Y_4 = 19/350 + 81\varepsilon/875 - 41009481\varepsilon^2/89600000$
$Y_5 = -257/8750 + 548953\varepsilon/3200000$

$T_1 = 0$
$T_2 = -1/4 - 9\varepsilon/160 - 135\varepsilon^2/1024 - 281637\varepsilon^3/1792000 - 417867903\varepsilon^4/1146880000$
$T_3 = 1/20 + 9\varepsilon/50 + 186381\varepsilon^2/896000 + 18689859\varepsilon^3/35840000$
$T_4 = -9/200 - 279\varepsilon/2240 - 1214757\varepsilon^2/3584000$
$T_5 = 193/7000 + 36873\varepsilon/280000$

Model B

$T_1 = 0$
$T_2 = -1/4 + b_1^2\varepsilon/40 + (77b_1^4 - 32b_1^3)\varepsilon^2/160 + (208031b_1^6 - 1124250b_1^5 + 15750b_1^4)\varepsilon^4/56000$
$Y_1 = -1 - 21b_1^2\varepsilon/10 - (243b_1^4 - 66b_1^3)\varepsilon^2/20 - (2350827b_1^6 - 1081500b_1^5 + 31500b_1^4)\varepsilon^3/28000$
$Y_2 = 1/5 + 133b_1^2/100 + (89228b_1^4 - 23905b_1^3)/7000$
$\quad + (125713264b_1^7 - 79898995b_1^5 + 9381750b_1^4)\varepsilon^3/210000$

ACKNOWLEDGMENT

This work was supported by the Office of Basic Energy Sciences, U.S. Departement of Energy, under Contract DE-FG02-87ER13648.

REFERENCE

1. J. M. Kincaid, M. Azadi, G. Fescos, L. Pellizzi, and K. B. Shon, Submitted for publication (1988).