

Note on the Perturbation Equation of State of Barker and Henderson*

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Perturbation theory of equation of state due to Barker and Henderson is reformulated. This new formulation makes it possible to calculate the Helmholtz free energy of a fluid system analytically by perturbation relations of Barker and Henderson, without use of any approximation or need of any numerical table for the hard-sphere reference system other than the original Percus-Yevick approximations. The results are compared with the calculation of Barker and Henderson, and it is shown that the two agree with each other at all the temperatures which are compared, while the present method produces compressibilities slightly closer to the experimental and machine-calculated data. The results of the present method, based on average Percus-Yevick hard-sphere compressibilities, are also compared with the result of other theories of equation of state of simple fluids, molecular dynamics, and Monte Carlo calculations.

I. INTRODUCTION

Perturbation equation of state of simple fluids due to Barker, Henderson, and co-workers has been probably a more successful approach to the prediction of equilibrium thermodynamic properties of simple real fluids,¹ classical and quantum, than other approaches so far published. The main objective of this perturbation approach is to calculate the properties of simple real fluids by perturbation around a reference hard-sphere fluid. For this purpose the macroscopic properties of the reference hard-sphere fluid should be as analytic as possible with respect to the molecular properties of hard spheres. While some satisfactory analytic relations are available for the hard-sphere equation of state, no satisfactory analytic form for the radial distribution function of the hard spheres, which is also needed in the perturbation equation of state of Barker and Henderson, is available. In the present paper a method is introduced by which this difficulty is eliminated.

II. REFORMULATIONS

Barker and Henderson¹ have shown that a perturbation approximation of the partition function of a system of simple spherical molecules with pairwise additive potential energy gives the following relation for Helmholtz free energy:

$$\begin{aligned} \Delta F/NkT &= (F - F_0)/NkT \\ &= 2\pi\rho\beta \int_{\sigma}^{\infty} g_0(d, R)u(R)R^2dR \\ &\quad - \pi\rho\beta \left(\frac{\partial\rho}{\partial P}\right)_0 \left(\frac{\partial}{\partial\rho}\right)_0 \rho \int_{\sigma}^{\infty} g_0(d, R)u^2(R)R^2dR. \quad (1) \end{aligned}$$

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¹ J. A. Barker, D. Henderson, and W. R. Smith, *J. Phys. Soc. Japan Suppl.* **26**, 284 (1969). Look for the other references in this paper.

In Eq. (1), $g_0(d, R)$ is the radial distribution function of a reference system of hard spheres with diameter d such that

$$d = \int_0^{\sigma} \{1 - \exp[-\beta u(R)]\} dR. \quad (2)$$

For $g_0(d, V)$, Barker and Henderson, in their earliest works,² used the tabulated numerical calculation of the Percus-Yevick equation³ for hard spheres for $2d < R \leq 3.95d$. For $d \leq R \leq 2d$, they used the related analytic expressions of Wertheim⁴; while for $R > 3.95d$, they approximated $g_0(d, R)$ to unity. Later Barker and Henderson calculated $g_0(R)$ for $d < R < 5d$ from $G(s)$, which is the Laplace transform of $Rg_0(d, R)$ and is derived by Wertheim,⁴ by numerical inversion,⁵ and again they approximated $g_0(d, R)$ to unity for $R \geq 5d$. Because of the difficulties for using tabulated values for $g_0(d, R)$ in integrals appearing in Eq. (1), and also because of the slow convergence of $g_0(d, R)$ toward unity, especially at high densities, use of the tabular values and numerical inversion of Laplace transform of $Rg_0(d, R)$ at best is cumbersome³ and at worst is unreliable.⁶ The following formulation makes it possible to use directly the analytic relations of $g_0^{(1)}(d, R)$ for $d \leq R \leq \sigma$ and $G(d, s)$ for $\sigma < R < \infty$.

Barker and Henderson,² Eq. (1), used the local compressibility approximation for the second-order perturbation term. In the present formulation we use the macroscopic compressibility approximation. As stated by Barker and Henderson, the use of either approximation does not change the over-all picture appreciably. The macroscopic approximation gives better agreement with machine-calculated data at low temperature, whereas the local approximation is slightly better at

² J. A. Barker and D. Henderson, *J. Chem. Phys.* **147**, 4714 (1967). See also: J. A. Barker and D. Henderson, *J. Chem. Educ.* **45**, 2 (1968); *J. Chem. Phys.* **46**, 2856 (1967).

³ G. J. Throop and R. J. Bearman, *J. Chem. Phys.* **42**, 2408 (1964).

⁴ M. S. Wertheim, *Phys. Rev. Letters* **10**, 8, 321 (1963).

⁵ S. Kim, D. Henderson, and J. A. Barker, *Can. J. Phys.* **47**, 99 (1969).

⁶ R. Bellman, *Numerical Inversion of the Laplace Transform* (American Elsevier Publ. Co., Inc., New York, 1966).

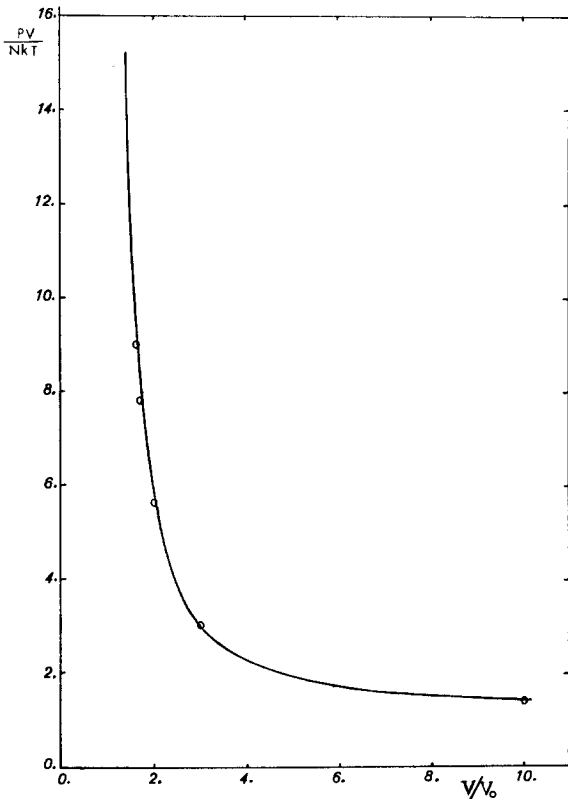


FIG. 1. Compressibility of hard spheres vs V/V_0 , ($V_0 = N\sigma^3/\sqrt{2}$), as calculated from the average Percus-Yevick equation; \circ are the molecular dynamic points for hard spheres.

high temperatures. In the present formulation, the macroscopic approximation is used to avoid double numerical differentiation of the second term with respect to density in deriving compressibility. The corresponding expression for the macroscopic approximation is given by

$$\frac{F - F_0}{NkT} = 2\pi\rho\beta \int_{\sigma}^{\infty} g_0(d, R)u(R)R^2dR - \pi\rho\beta \left(\frac{\partial\rho}{\partial P}\right)_0 \int_{\sigma}^{\infty} g_0(d, R)u^2(R)R^2dR. \quad (3)$$

The integral in the first term, in the right-hand side of Eq. (3) can be written as

$$\int_{\sigma}^{\infty} g_0(d, R)u(R)R^2dR = \int_d^{\infty} g_0(d, R)u(R)R^2dR - \int_d^{\sigma} g_0(d, R)u(R)R^2dR. \quad (4)$$

According to Frisch *et al.*⁷ by defining $G(d, s)$ and

$U_1(c, s)$ such that

$$G(d, s) = \int_1^{\infty} e^{-sx} g_0(d, x)xdx \quad (5)$$

and

$$xu(c, x) = \int_0^{\infty} e^{-sx} U_1(c, s)ds, \quad (6)$$

where $x = R/d$ and $c = d/\sigma$, the first term in the right-hand side of Eq. (4) can be written as

$$\int_d^{\infty} g_0(d, R)u(R)R^2dR = d^3 \int_0^{\infty} G(d, s)U_1(c, s)ds. \quad (7)$$

The Laplace transform form of $Rg_0(d, R)$, that is, $G(d, s)$, as defined by Relation (5) has been derived analytically by Wertheim⁴ from Percus-Yevick integral equation for hard spheres and is given in the Appendix of the present paper. The inverse Laplace transform of $xu(c, x)$, that is $U_1(c, s)$, is defined by Eq. (6).

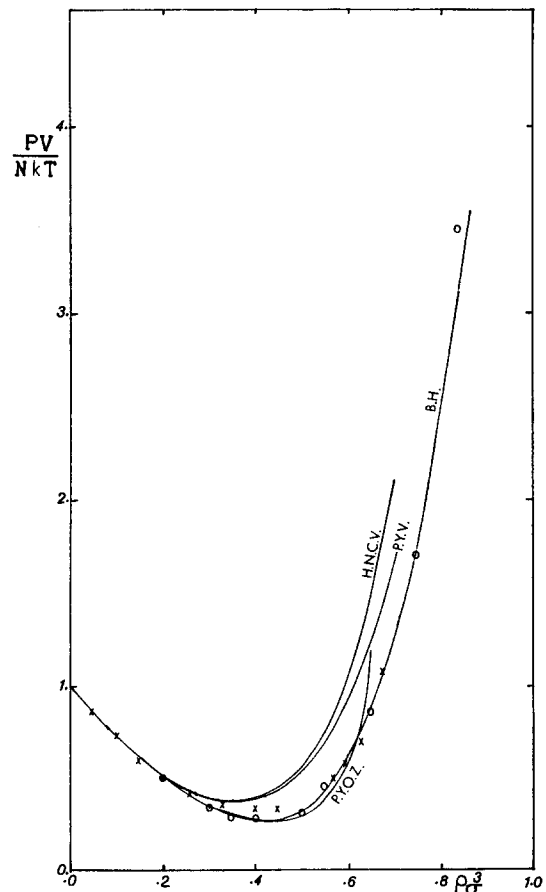


FIG. 2. Equation of state for 6,12 potential at $T^* = 1.35$. The curves are isotherms calculated by different theories: HNCV, Hypernetted chain and virial theorem; PYV, Percus-Yevick and virial theorem; BH, Barker and Henderson's perturbation method; PYOZ, Percus-Yevick and Ornstein-Zernike; BGV, Born-Green and virial theorem. The points given by \circ , and \bullet are machine-calculated values. The points given by \times are experimental values. See Ref. 2.

⁷ H. L. Frisch, J. L. Katz, E. Praestgaard, and J. L. Lebowitz, *J. Phys. Chem.* **70**, 2016 (1966).

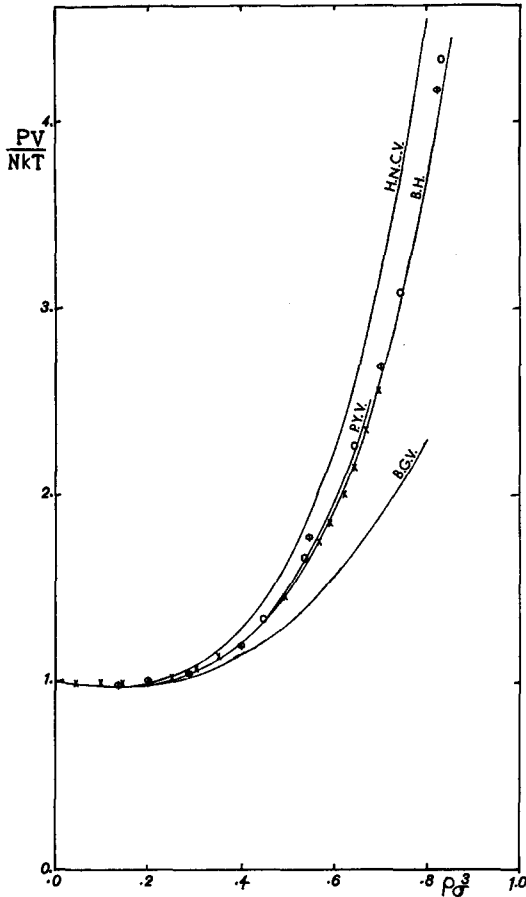


FIG. 3. Equation of State for the 6,12 potential at $T^*=2.74$. The curves are isotherms calculated by different theories as labeled. The points given by \circ , \emptyset , and \bullet are machine-calculated values. The points given by \times are experimental values. See Ref. 2.

Considering Lennard-Jones (12,6) potential function

$$u(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6],$$

it is clear that the hard-sphere diameter d as defined by Eq. (2) is always less than or equal to σ . Also, it can be shown, for $T^* = kT/\epsilon \leq 0(10^4)$, that

$$d \geq \sigma/2$$

or

$$d \leq \sigma \leq 2d.$$

With this constraint the upper limit of the second integral in the right-hand side of Eq. (4) will not exceed $2d$. For $d \leq R \leq 2d$, $g_0^{(1)}(d, R)$ also is calculated analytically by Wertheim. A form of $g_0^{(1)}(d, R)$ which contains only real variables is given in the Appendix of the present paper.

Similarly, the integral in the second term of Eq. (3) can be divided into two integrals as the first term. By defining $U_2(d, s)$ as the inverse Laplace transform of $x u^2(c, x)$ one finally gets

$$\frac{\Delta F}{NkT} = \frac{6\eta}{T^*} \left[2(I_1 - I_2) - \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_0 \frac{1}{T^*} (I_3 - I_4) \right], \quad (8)$$

where

$$\eta = \frac{1}{6} \pi \rho d^3,$$

$$I_1(d, c) = \int_0^\infty G(d, s) U_1(c, s) ds,$$

$$I_2(d, c) = \int_1^{1/c} g_0^{(1)}(d, x) u(c, x) x^2 dx,$$

$$I_3(d, c) = \int_0^\infty G(d, s) U_2(c, s) ds,$$

and

$$I_4(d, c) = \int_1^{1/c} g_0^{(1)}(d, x) u^2(c, x) x^2 dx, \quad (9)$$

and where

$$U_1(c, s) = \frac{4}{c^6} s^4 \left[\frac{1}{10!} \left(\frac{s}{c} \right)^6 - \frac{1}{4!} \right]$$

and

$$U_2(c, s) = \frac{16}{c^{12}} s^{10} \left[\frac{1}{22!} \left(\frac{s}{c} \right)^{12} - \frac{2}{16!} \left(\frac{s}{c} \right)^6 + \frac{1}{10!} \right]. \quad (10)$$

From thermodynamic relations for pure systems, the compressibility can be derived from the Helmholtz free energy by

$$Z = PV/NkT = \rho(\partial/\partial\rho)(F/NkT)_T \quad (11)$$

By inserting Eq. (8) in Eq. (11) we get

$$\begin{aligned} \frac{PV}{NkT} &= \left(\frac{PV}{NkT} \right)_0 \\ &+ \frac{6\eta}{T^*} \left\{ 2(I_1 - I_2) - \frac{1}{T^*} \left[\frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_0 + \frac{\rho}{\beta} \left(\frac{\partial^2 \rho}{\partial P^2} \right)_0 \right] (I_3 - I_4) \right\} \\ &+ \frac{6\eta}{T^*} \left[2(I_1' - I_2') - \frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_0 \frac{\rho}{T^*} (I_3' - I_4') \right], \quad (12) \end{aligned}$$

where $(PV/NkT)_0$ is the hard-sphere compressibility and

$$I_1'(d, c) = \int_0^\infty f(s, \eta) U_1(c, s) ds,$$

$$I_2'(d, c) = \int_1^{1/c} \frac{\partial g_0^{(1)}(d, x)}{\partial \rho} u(c, x) x^2 dx,$$

$$I_3'(d, c) = \int_0^\infty f(s, \eta) U_2(c, s) ds,$$

$$I_4'(d, c) = \int_1^{1/c} \frac{\partial g_0^{(1)}(d, x)}{\partial \rho} u^2(c, x) x^2 dx, \quad (13)$$

and $f(s, \eta)$ is given in the Appendix.

Equation (12) has an advantage over the Barker and Henderson approach in that it is completely analytic, i.e., no tabular values or approximations are needed for $g_0(d, x)$ except the Percus-Yevick original

TABLE I. Compressibilities of Lennard-Jones 12,6 fluid for different isotherms.

ρ^*	$T^*=2.74$		$T^*=1.35$		$T^*=1.00$		$T^*=0.722$	
	a	b	a	b	a	b	a	b
0.05	0.98288	0.98245	0.86047	0.85870	0.76638	0.76307	0.61421	0.60771
0.10	0.97428	0.97305	0.73395	0.72875	0.55279	0.54306	0.26556	0.24642
0.15	0.97533	0.97330	0.61866	0.61018	0.35371	0.33783	-0.05970	-0.09092
0.20	0.98780	0.98521	0.51489	0.50424	0.16702	0.14713	-0.36905	-0.40808
0.25	0.01413	1.01131	0.42457	0.41336	-0.00661	-0.02749	-0.66510	-0.70599
0.30	1.05739	1.05471	0.35122	0.34118	-0.16418	-0.18278	-0.94658	-0.98286
0.35	1.12136	1.11915	0.29981	0.29258	-0.30050	-0.31374	-1.20874	-1.23434
0.40	1.21056	1.20912	0.27685	0.27383	-0.40825	-0.41350	-1.44368	-1.45339
0.45	1.33039	1.32992	0.29046	0.29272	-0.47792	-0.47315	-1.64034	-1.63016
0.50	1.48720	1.48781	0.35060	0.35882	-0.49761	-0.48151	-1.78436	-1.75165
0.55	1.68850	1.69019	0.46926	0.48371	-0.45272	-0.42479	-1.85775	-1.80135
0.60	1.94310	1.94579	0.66083	0.68137	-0.32559	-0.28593	-1.83845	-1.75867
0.65	2.26142	2.26490	0.94255	0.96862	-0.09494	-0.04457	-1.69967	-1.59825
0.70	2.65571	2.65969	1.33497	1.36561	0.26477	0.32416	-1.40905	-1.28911
0.75	3.14048	3.14453	1.86271	1.89656	0.78422	0.85024	-0.92758	-0.79357
0.80	3.73292	3.73650	2.55523	2.59056	1.50027	1.56987	-0.20825	-0.06582
0.85	4.45344	4.45592	3.44791	3.48262	2.45731	2.52685	0.80564	0.94980
0.90	5.32642	5.32703	4.58338	4.61507	3.70896	3.77430	2.18272	2.32113
0.95	6.38105	6.37888	6.01319	6.03924	5.32018	5.37692	4.00621	4.13105
1.00	7.65240	7.64648	7.79988	7.81764	7.36999	7.41376	6.37744	6.48108
1.05	9.18286	9.17214	10.01968	10.02667	9.95486	9.98165	9.42022	9.49570

^a Present work based on the Padé approximant of Ree and Hoover² for the hard-sphere compressibility.

^b Calculated by Barker and Henderson (private communication) based

on the Padé approximant of Ree and Hoover for the hard-sphere compressibility, and approximation of $g_0(d, R)$ to unity for $R \geq 5d$.

approximation. Barker and Henderson have used the Padé approximant of Ree and Hoover for $(PV/NkT)_0$. It is also possible to use the arithmetic average of the two equations of state for hard-sphere system which were derived by Thiele⁸ from the Percus-Yevick integral equation by using virial and Ornstein-Zernike relations, namely

$$(PV/NkT)_0 = (1 + \eta + \eta^2 - 1.5\eta^3)/(1 - \eta)^3. \quad (14)$$

This average relation, besides having a good match with machine calculations as shown in Fig. 1, makes possible the comparison of the perturbation around the hard-sphere Percus-Yevick equation with the Lennard-Jones Percus-Yevick calculation.⁹⁻¹¹ Then from (14) the compressibility coefficient for hard spheres is

$$\frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_0 = \frac{(1 - \eta)^4}{(1 + 2\eta)^2 - 1.5\eta^3(4 - \eta)} \quad (15)$$

and

$$\frac{\rho}{\beta} \left(\frac{\partial^2 \rho}{\partial P^2} \right)_0 = \frac{2\eta(5\eta^2 - 10\eta - 4)}{(1 - \eta)^5} \left[\frac{1}{\beta} \left(\frac{\partial \rho}{\partial P} \right)_0 \right]^2. \quad (16)$$

⁸ E. Thiele, J. Chem. Phys. **30**, 474 (1963).

⁹ L. Verlet and D. Levesque, Physica **36**, 254 (1967).

¹⁰ D. Levesque, Physica **32**, 1985 (1966).

¹¹ Recently, Carnahan and Starling showed that

$$(PV/NkT)_0 = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3$$

is in a better agreement with machine-calculated data for hard spheres than even the Padé approximant of Ree and Hoover while this has much simpler form than the Padé approximant. [N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969)].

III. RESULTS

The necessary computations are performed by GE 430 time-sharing computer. The integrations are done numerically by Simpson's rule and the accuracy is checked by changing and decreasing the interval widths in the integrations. Table I presents a comparison of the results of the present analytical formulation with the results of Barker and Henderson at reduced densities for four different isotherms. Both of the results are calculated by using Padé approximant of Ree and Hoover for the hard-sphere compressibility. The compressibility coefficient of the hard spheres, and its derivative with respect to density, are calculated from (Percus-Yevick)-(Ornstein-Zernike) compressibility relation.^{4,8} As can be easily seen from Table I, the values of the compressibilities of Lennard-Jones (12, 6) potential calculated by the present method are slightly lower than the values calculated by Baker and Henderson at high densities and are slightly closer to the experimental and machine-calculated data. The difference between the results of the two methods increases at lower temperatures. This difference could be very well due to the difference between the local compressibility and macroscopic compressibility approximations which are used in the two methods for the coefficient T^{*-2} in the relation of the Helmholtz free energy respectively.

Figures 2 and 3 show the compressibility of Lennard-Jones (12, 6) fluid as calculated by different theories versus density. For the perturbation curve Eqs. 14-16 are used to compare the perturbation around the Percus-Yevick equation for hard spheres with the direct solution of Percus-Yevick equation for Lennard-Jones

potential. The comparison indicates that while Percus-Yevick equation for Lennard-Jones potential is as good as perturbation calculations for Lennard-Jones around hard-sphere system at high temperatures, the former diverges at low temperatures, while the latter does not.

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APPENDIX

Laplace Transform of $g_0(d,x)x$ is given by

$$G(d,x) = \{sL(s)e^{-s}/[12\eta L(s)e^{-s} + S(s)]\}.$$

The derivative of $\rho G(d,x)$ with respect to density is given by

$$f(s,\eta) = \frac{s^4 e^{-s} [s(1+\eta-2\eta^2) + (2\eta+1)^2]}{[12\eta L(s)e^{-s} + S(s)]^2},$$

where

$$L(S) = (1 + \frac{1}{2}\eta)s + (1 + 2\eta)$$

and

$$S(s) = (1-\eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1+2\eta).$$

$g_0^{(1)}(d,x)$ as a function of only real variables is:

$$g_0^{(1)}(d,x) = [3x(1-\eta)^2]^{-1} \times [(H_0 + H_1 + H_2) \exp(A_1) + \exp(A_3)(2D_1 \cos A_2 - 2D_2 \sin A_2)],$$

$$A_1 = [2\eta/(1-\eta)](x-1)[-1+x_+ + x_-],$$

$$A_2 = [2\eta/(1-\eta)](x-1)(3^{1/2}/2)(x_+ - x_-),$$

$$A_3 = [2\eta/(1-\eta)](x-1)[-1 - 0.5(x_+ + x_-)],$$

$$D_1 = H_0 - 0.5(H_1 + H_2),$$

$$D_2 = (3^{1/2}/2)(H_1 - H_2),$$

$$H_0 = 1 + \frac{1}{2}\eta,$$

$$H_1 = [-1/4\eta(f^2 + \frac{1}{8})^{1/2}]$$

$$[x_-^2(1 - 3\eta - 4\eta^2) + x_+(1 - \frac{5}{2}\eta^2)],$$

$$H_2 = [1/4\eta(f^2 + \frac{1}{8})^{1/2}]$$

$$[x_+^2(1 - 3\eta - 4\eta^2) + x_-(1 - \frac{5}{2}\eta^2)],$$

$$x_+ = [f + (f^2 + \frac{1}{8})^{1/2}]^{1/3},$$

$$x_- = -[|f - f^2 + \frac{1}{8}|^{1/2}]^{1/3},$$

$$f = (3 + 3\eta - \eta^2)/4\eta^2.$$