

## **Khasare's equation of state for Hard-Sphere and Lennard-Jones pure fluids, using Computer Algebra**

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### **ABSTRACT**

*Present work uses the concept of scaled particle along with perturbation and a variation approach, to develop an equation of state EOS, for a mixture of hard sphere HS, Lennard-Jones LJ fluids. A suitable flexible functional form for radial distribution function  $G(r)$  is assumed for the pure, with cavity radius parameter  $r$  as a variable. The function  $G(r)$  has an arbitrary parameter  $m$  and the self-consistent parameter  $k_c$ . Different EOS can be obtained with a suitable choice of  $m$ . For  $[m = 0.75, k_c = 0]$  and  $[m = 0.80, k_c = 0.058]$  results are close to molecular dynamics MD for pure HS and LJ fluid respectively.*

**Key Words:** Equation of State (EOS), (LJ) Potential, Hard-Sphere (HS) Potential, liquid mixture, Computer Simulation.

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### **INTRODUCTION**

The hard sphere can serve as a basic reference system for many perturbation and variation theories [1- 7]. With suitable approximations, bulk and structural properties of liquids may be studied. The two parameters  $\sigma$  and  $\epsilon$  are related to molecular diameter and the binding energy respectively of the molecule. In perturbation and variation theories it is observed that, at high temperatures only repulsive part of potential is prominent, while at lower temperatures the attractive part becomes appreciable.

For pair wise additive intermolecular potentials, all the thermodynamic functions may be expressed, in terms of the radial distribution functions (RDF). The expressions are particularly simple for hard-core fluids, since in that case the internal energy reduces to that of an ideal gas, while in the pressure equation it is only the contact values, rather than the full (RDF) which appear explicitly. Therefore, knowledge of the contact values  $g(\sigma)$  of the (RDF) in hard-core fluids where  $(\sigma)$  is the separation at contact, between the centers of two interacting fluid particles, suffices to obtain the equation of state (EOS) of these systems.

In present formulation, (EOS) and expressions for the contact values of the (RDF) are determined in a unique way. The use of a precise and well defined probability distribution function [8- 12] in a perturbation theory opens up, the

possibility of deriving a closed theoretical scheme for the determination of thermodynamic properties of a more realistic model. The current formulation assumes surface tension, as some arbitrary function of solute cavity radius ( $r$ )

Present paper is organized as follows. In Section 2.1 partition function approach is used for computation of probability distribution function and related work done. Section-2.2 deals with thermodynamic work done. Equation of state and expression for surface tension has been derived using algebra. The necessary calculation is presented in section-2.3. Section-3 is devoted for the results corresponding to different value of an arbitrary parameter ( $m$ ) and the self-consistent parameter ( $k_c$ ). Lastly section-4 is devoted for the discussion and conclusion pertaining to the derived equation of state.

### Formulation of work done

Consider the formation in a hard sphere fluid of a cavity of radius ( $r$ ) Let  $[pG(r, \rho)]$  be the concentration of the centers of the spheres on the surface of the cavity. The cavity plays exactly the role of the hard sphere of diameter  $[2r-d]$ , since it excludes the centers of other particles from the spherical region. The function  $G(r)$  may be calculated through the thermodynamic probability considerations.  $[dp_c(r) = 4\pi r^2 \rho G(r) dr]$  is the conditional probability that a particle is found in the spherical shell of thickness  $dr$  at distance  $r$  from the center of the cavity. The probability that a cavity of radius  $[r < d/2]$  is empty is  $[p(r) = 1 - (4/3)\pi r^3 \rho]$ , since one particle, at most, may be located there.

The probability, that a spherical shell contains the molecule may be represented as

$$dp(r) = -p(r) dp_c(r), dp(r) = -p(r) \rho G(r) [4\pi r^2 dr]$$

Above two expressions for (HS) lead to

$$G(r) = \frac{1}{\left[1 - \frac{4\pi r^3 \rho}{3}\right]}, r < \frac{d}{2}$$

### Work done for ( $r < d/2$ ):

Let us consider a cavity of volume ( $v$ ) in liquid having volume ( $V$ ) about, a specific point. The probability  $p(v)$  of finding a molecule in the cavity may be expressed as

$$p(v) = v \rho, \rho = \frac{N}{V}, p_c = [1 - p(v)]$$

And the probability of cavity being empty is  $p_c$ .

We state general expression for probability  $p(d)$  for cavity being empty as under

$$p(d) = \frac{\int_0^R e^{(-\beta u(r))} [4\pi r^2] dr}{\int_0^R [4\pi r^2] dr}, R = \left[\frac{3V}{4\pi}\right]^{(1/3)}, \beta = \frac{1}{k_B T} \quad (1)$$

In above equation interaction pair-potential  $u(r)$  can be treated as hard sphere potential  $u_{HS}$  if ( $r < d$ ), and  $u(r)$  is treated as  $u_{LJ}$ , potential for ( $r > d$ )

Therefore we have the interaction pair-potential,

$$u(r) = u_{HS}, r < d, u(r) = u_1(r), d \leq r \quad (2)$$

$$u_1(r) = 4 \epsilon \left[ \frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right], \sigma = \alpha d, BE = \epsilon$$

And BE=epsilon is depth of LJ potential alpha relates HS parameter d to the corresponding LJ parameter sigma.

With the help of hard sphere potential, we define following heaviside function as follows.

$$e^{(-\beta u_{HS})} = \text{Heaviside}(r - d) \quad (3)$$

$$\text{Heaviside}(r - d) = 0, r < d, \text{Heaviside}(r - d) = 1, d \leq r$$

Now p(d) is evaluated using algebra, by removing higher order terms  $O(d^6)$ . The expression for a probability p(d) is stated as sum of two parts,  $p_0(d)$  namely for hard sphere potential and  $[p_1(d)$  and  $p_2(d)]$  are grouped together as LJ potential.

$$p(d) = p_0(d) + [p_1(d) + p_2(d)], p(d) = 1 - \frac{N d^3 f(\beta \epsilon)}{R^3}$$

Where  $p_0(d)$  is related to hard sphere parameter d, and  $[p_1(d), p_2(d)]$  are related to the variable epsilon and d

$$p_0(d) = \left[ 1 - \frac{N d^3}{R^3} \right], p_1(d) = \left[ \frac{F_1 N d^3}{R^3} \right], p_2(d) = \left[ \frac{F_2 N d^3}{R^3} \right]$$

$$F_1(\alpha) = \frac{4(\alpha^6 - 3)\beta \epsilon \alpha^6}{3}, F_2(\alpha) = -\frac{8}{105} \beta^2 \epsilon^2 \alpha^{12} [15 \alpha^{12} - 42 \alpha^6 + 35]$$

$$f(\beta \epsilon) = 1 - F_1(\alpha) - F_2(\alpha)$$

For hard sphere,  $p_0(r)$  is probability [7] that a cavity is empty.

General expression for probability p(r) can be now as under.

$$p(r) = p_0(r) + [p_1(r) + p_2(r)], p(r) = 1 - \frac{N r^3 f(\beta \epsilon)}{R^3}, r \leq \frac{d}{2} \quad (4)$$

And the probability that a spherical shell contains the molecule may be represented as

$$dp(r) = -p(r) dp_c(r), dp(r) = -p(r) \rho G(r) [4 \pi r^2 dr]$$

Where

$$p_0(r) = \left[ 1 - \frac{N r^3}{R^3} \right], p_1(r) = \left[ \frac{F_1 N r^3}{R^3} \right], p_2(r) = \left[ \frac{F_2 N r^3}{R^3} \right]$$

$$p_0(r) = \left[ 1 - \frac{4 \pi r^3 \rho}{3} \right], p_1(r) = \left[ \frac{F_1(\alpha) N r^3}{R^3} \right], p_2(r) = \left[ \frac{F_2(\alpha) N r^3}{R^3} \right]$$

In terms of reduced number density [ $\eta = (\pi/6)\rho d^3$ ], number density, [ $\rho = N/V$ ], and  $N$  is the Avogadro number, above equation can be expressed as

$$p(r) = p_0(r) + [p_1(r) + p_2(r)], p(r) = 1 - \frac{8 \eta r^3 f(\beta \epsilon)}{d^3}, r \leq \frac{d}{2} \quad (5)$$

Where

$$p_0(r) = \left[ 1 - \frac{8 \eta r^3}{d^3} \right], p_1(r) = \left[ \frac{8 F_1(\alpha) \eta r^3}{d^3} \right], p_2(r) = \left[ \frac{8 F_2(\alpha) \eta r^3}{d^3} \right]$$

The relation [6] gives the reversible work

$$\beta W(r) = -\ln(p(r)), r \leq \frac{d}{2} \quad (6)$$

$W(r)$ , necessary to create a cavity of radius  $r$  in the real fluid.  $p(r)$ ,  $W$  and  $G$  depend exclusively upon  $[r, \eta, \epsilon]$ .  $W(r)$  is obtained by removing higher order terms  $[O(\eta^2)]$ , and split into two parts as follows.

$$\beta W = \beta W_0 + [\beta W_1 + \beta W_2], r \leq \frac{d}{2} \quad (7)$$

$$\beta W_0(r) = -\ln\left(1 - \frac{8 \eta r^3}{d^3}\right), \beta W_1(r) = \left[\frac{8 F_1(\alpha) \eta r^3}{d^3}\right], \beta W_2(r) = \left[\frac{8 F_2(\alpha) \eta r^3}{d^3}\right]$$

$W_0$  corresponds to hard sphere interaction potential, while  $[W_1, W_2]$  relates to perturbing LJ potential part.

Expression for  $[(dW_0/dr), (dW_1/dr), (dW_2/dr)]$  can be written as

$$\frac{\beta dW_0}{dr} = \frac{24 \eta r^2}{d^3 \left[ 1 - \frac{8 \eta r^3}{d^3} \right]}, \frac{\beta dW_1}{dr} = \frac{24 \eta F_1(\alpha) r^2}{d^3}, \frac{\beta dW_2}{dr} = \frac{24 \eta F_2(\alpha) r^2}{d^3}$$

Normally  $W(r)$  is related to the thermodynamic work done against external force (pressure) and internal force (surface tension). Combining two equations eq. (4) and eq. (6) we have.

$$\frac{dp}{p} = -\beta dW, \frac{dp}{p} = -4 \pi \rho G(r) r^2 dr, r \leq \frac{d}{2} \quad (8)$$

Now we can express  $G(r)$  as

$$G(r) = -\frac{\beta \left[ \frac{dW}{dV} \right]}{\rho}, G(r) = \frac{1}{\left[ 1 - \frac{8 \eta r^3}{d^3} \right]} - F_1(\alpha) - F_2(\alpha), r \leq \frac{d}{2} \quad (9)$$

## 2.2 Work done for $r > d/2$ :

Work done is stated as

$$dW(r) = P dV - S dA, dW(r) = k_B T \rho G(r) dV \quad (10)$$

Here  $[dA]$  and  $[dV]$  is increase in surface area and volume respectively.

For real fluid, hard sphere potential along with perturbing potential LJ contributes effective net positive value for surface tension  $S$ .

Therefore, from above equation we have following expression for  $G(r)$ .

$$G(r) = \frac{\left[ P - \frac{2S}{r} \right]}{\rho k_B T} \quad (11)$$

But an equation of state for a fluid in terms of hard sphere diameter  $d$  and binding energy epsilon is expressed [7] as

$$\frac{\beta P}{\rho} = [1 + 4 \eta g(d)] \quad (12)$$

In order to achieve *more accurate EOS for LJ fluid at critical temperature over entire reduced density range* than Barker-Henderson result[1,3,7] and earlier result[13-15], found following condition as given below.

$$g(d) = G(ge d), ge = e^{(-k_c [F_1(\alpha) + F_2(\alpha)] \eta)} \quad (13)$$

Because empty sphere of radius  $d$  affects the remainder of the fluid precisely like another molecule, and  $[ge]$  is self-consistent function. If  $[k_c = 0]$  then we have old condition  $[g(d) = G(d)]$ .

Thus eq. (12) can be written as

$$\frac{\beta P}{\rho} = [1 + 4 \eta G(ge d)] \quad (14)$$

To proceed further, we need to know the dependence of  $r$  on surface tension  $S(r)$ . For surface tension,  $r$  is not too small but finite.

We assume [9] following expression.

$$S(r) = S_0 \left[ 1 + 2 \delta \left( \frac{d}{r} \right)^m \right], \frac{d}{2} \leq r \quad (15)$$

Surface tension, suggested by Kirkwood and Buff [10] can be obtained for [m =1] as.

$$S(r) = S_0 \left[ 1 + \frac{2 \delta d}{r} \right], \frac{d}{2} \leq r \quad (16)$$

(Scaled Particle Theory, page 618 eq.(5.8) )Rev. Mod. Phys, 48,(1976).)

Here efforts are taken to obtain the EOS by using algebra. As a starting point, we assume following functional form.

$$S(r) = A + B \left[ \frac{m r^2}{d^2} - \frac{(1+m) r}{d} \right], \frac{d}{2} \leq r \quad (17)$$

Where, [A] and [B] are constants to be determined.

On substitution of S(r), we get corresponding G(r) as given below.

$$G(r) = \frac{\beta P}{\rho} - \frac{A d}{r} + \left[ 1 + m - \frac{m r}{d} \right] B, \frac{d}{2} \leq r$$

For [r/d = ge] we have following result.

$$G(ge d) = \frac{\beta P}{\rho} - \frac{A}{ge} + [1 + m - ge m] B, \frac{d}{2} \leq r$$

#### Evaluation of [A] and [B]:

We use condition of continuity [G(r) and dG(r)/dr] for the evaluation of [A] and [B] at [r=d/2 ](contact point). We have expression for G(r).

$$G(r) = \frac{1}{\left[ 1 - \frac{8 \eta r^3}{d^3} \right]} - F_1(\alpha) - F_2(\alpha), r \leq \frac{d}{2}$$

We also have following expressions for G(r) as below.

$$G(r) = -\frac{1}{-1 + 4 \eta} + \left[ \frac{4 \eta}{ge (-1 + 4 \eta)} - \frac{d}{r} \right] A + \left[ \frac{4 \eta m (ge - 1)}{-1 + 4 \eta} - \frac{m r}{d} + 1 + m - \frac{4 \eta}{-1 + 4 \eta} \right] B, \frac{d}{2} \leq r \quad (18)$$

The values for [A] and [B] are worked out using computer algebra as under.

$$A = asol0 + asol1, B = bsol0 + bsol1 \quad (19)$$

Where

$$asol0 := \frac{1}{4} (4 m a_1 F_1 \eta^3 + 4 m a_2 F_2 \eta^3 + 24 ge \eta^2 m - 15 \eta^2 m - 9 m a_2 F_2 \eta^2 - 9 m a_1 F_1 \eta^2 + 6 m a_2 F_2 \eta - 6 \eta + 6 m a_1 F_1 \eta - m a_1 F_1 - m a_2 F_2) ge / ((\eta - 1)^2 (-4 ge \eta m + 4 \eta ge^2 m + \eta m - ge))$$

$$asol1 := \frac{1}{4} \frac{ge (-1 + 4 \eta) m F_1}{-4 ge \eta m + 4 \eta ge^2 m + \eta m - ge}$$

$$bsol0 := (4 a_2 F_2 ge \eta^3 - 9 a_1 F_1 ge \eta^2 - 6 \eta^2 - a_1 F_1 ge - a_2 F_2 ge + 6 a_1 F_1 ge \eta + 9 ge \eta^2 + 6 a_2 F_2 ge \eta + 4 a_1 F_1 ge \eta^3 - 9 a_2 F_2 ge \eta^2) / ((\eta - 1)^2 (-4 ge \eta m + 4 \eta ge^2 m + \eta m - ge))$$

$$bsol1 := \frac{(-1 + 4 \eta) F_1 ge}{-4 ge \eta m + 4 \eta ge^2 m + \eta m - ge}$$

[Zero] represents reference potential, and [One] is used for perturbing LJ potential.

Equation of state for model fluid can now be stated as

$$\frac{\beta P}{\rho} = eq, eq = eq0 + eq1 \quad (20)$$

In above equation if perturbing LJ potential is absent then equation is obtained for hard sphere liquid. On the other hand if we introduce perturbing LJ potential, equation represents the LJ liquid only and hard sphere reference potential does not have any role to play.

$$eq0 := \frac{-ge + (m + (-2 - 4 m) ge + 4 ge^2 m) \eta + (6 + 2 m + (-9 - 8 m) ge + 8 ge^2 m) \eta^2}{((-4 ge m + 4 ge^2 m + m) \eta - ge) (1 - \eta)^2} \quad (21)$$

$$eq1 := \frac{(4 ge^2 m - 4 ge m - 4 ge + m) \eta (F_1 + F_2)}{-4 ge \eta m + 4 \eta ge^2 m + \eta m - ge} \quad (22)$$

## RESULTS

In this section we have carried out the comparative study of compressibility factor Z for different EOS. Results are presented in tabular form for hard sphere (Table-1) as well as for Lennard-Jones liquid (Table-2).

Z1 = Z(SBK) = [eq0<sub>m=0.75</sub>], Z2 = Z(CS) be denoting different EOS in the (Table-1) and

Z1 = Z(SBK) = [eq0<sub>m=0.80</sub> + eq1<sub>m=0.80</sub>], Z2=Z(BH2), be denoting different EOS in the Table-2 only.

**Case A: Hard Sphere Potential**

Comparative study of (Table-1) suggest that EOS presented for gives values of Z(SBK) well in agreement with Z(MD).

$$Z(SBK) = eq0, m = \frac{3}{4}, Z(CS) = \frac{[1 + \eta + \eta^2 - \eta^3]}{(1 - \eta)^3} \quad (23)$$

**Table-1: Equation of State (EOS)for Hard-Sphere potential [m = 0.75, k<sub>c</sub> = 0]**

S.No,	eta,	Z(SBK),	Z(MD),	Z(CS)
1,	0.052,	1.24,	1.24,	1.240
2,	0.105,	1.55,	1.55,	1.550
3,	0.157,	1.97,	1.97,	1.970
4,	0.209,	2.52,	2.52,	2.520
5,	0.262,	3.27,	3.27,	3.260
6,	0.314,	4.30,	4.29,	4.280
7,	0.367,	5.74,	5.71,	5.710
8,	0.419,	7.79,	7.73,	7.750
9,	0.471,	10.77,	10.70,	10.750
10,	0.524,	15.26,	15.00,	15.300

**3.2 Case B: Lennard-Jones (L-J) potential**

The comparison in Table-2 shows the closeness of values of Z with molecular dynamics Z(MD) results.

For [m=0.80,  $\alpha = (3/2)^{(1/6)}$ ] we have following results for equation of state.

$$\frac{\beta P}{\rho} = Z, Z = eq0 + eq1, m = 0.80, ge = e^{\left(-k_c \left[-3\beta\epsilon - \frac{69}{70}\beta^2\epsilon^2\right]\eta\right)}, k_c = 0.58 \quad (24)$$

With a critical constant are given below.

$$\beta\epsilon_c = 0.750242034658, \eta_c = 0.157972241500 \quad (25)$$

It is observed that [rms-deviation<sub>(SBK)</sub> = 0.036835], while [rms-deviation<sub>(BH)</sub> = 0.041593].

**Table-2: Equation of State (EOS) for Lennard-Jones fluid [m = 0.80, k<sub>c</sub> = 0.58]**

S.No,	eta,	Z(MD),	Equ[m0],	Z(BH)
1,	0.052,	0.72,	0.75,	0.740
2,	0.105,	0.50,	0.54,	0.520
3,	0.157,	0.35,	0.38,	0.360
4,	0.209,	0.27,	0.30,	0.260
5,	0.262,	0.30,	0.35,	0.270
6,	0.288,	0.41,	0.45,	0.350
7,	0.340,	0.80,	0.87,	0.740
8,	0.393,	1.73,	1.73,	1.640
9,	0.445,	3.37,	3.35,	3.360
10,	0.497,	6.32,	6.33,	6.320



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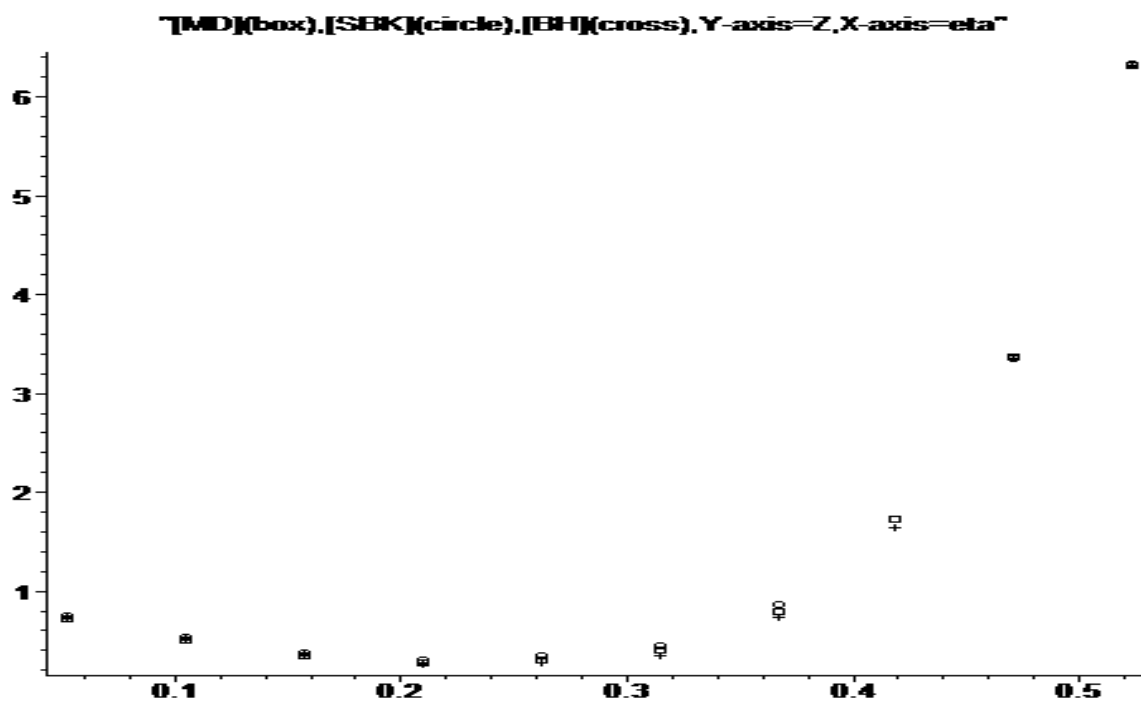
**CONCLUSION**

It is thus seen that, we have same mathematical result, for physical property such as compressibility factor  $[(\beta P/p) = Z \text{ (SBK)}]$ , which corresponds to present axiomatic form. With  $[m = 0.75, k_c = 0]$  and  $[m = 0.80, k_c = 0.58]$  for  $Z$  (HS),  $Z$  (LJ) in above formulation, for entire density region there is close agreement (see appendix) with  $Z$  (MD) results.

**REFERENCES**

- [1] Barker J.A. and Henderson D, J. Chem. Phys, (1967), **47**, 4714.
- [2] Weeks J.D. Chandler D and Henderson H.C, J. Chem. Phys. (1971), **45**, 5422.
- [3] Henderson D. and Barker J.A, J. Chem. Phys, (1968), **49**, 3377.
- [4] Mansoori G.A. and Canfield F.B, J. Chem. Phys, (1969), **51**, 4958.
- [5] Mansoori G.A. and Canfield F.B., J. Chem. Phys, (1970) **53**, 1618.
- [6] Mansoori G.A. Carnahan N.F. Starling K.B. and Leland T.W. J. Chem. Phys, (1971) **54**, 1523.
- [7] Barker J.A. and Henderson D, Rev. Mod. Phys, (1976), **48**, 587.
- [8] Reiss H, Frisch H.L. and Lebowitz J.L, J. Chem. Phys, (1959), **31**, 369.
- [9] Khasare S.B, Indian J Pure and Appl Phys. (1988), **26**, 487.
- [10] Kirkwood J.G. and Buff F.P, J. Chem. Phys, (1949), **17**, 338.
- [11] Khasare S.B, Indian J Pure and Appl. Phys, (1996), **34**, 448.
- [12] Khasare S.B. Modern Physics Letters B, (MPLB), (2008), **22**, No.26 2601.
- [13] Khasare. S.B. and Deshpande. M.S, Pramana J of Physics, (2011), **76**, No.6, 901.
- [14] Khasare. S.B, Chin. Phys. B, (2011), **20**, No.8, 085101.
- [15] Khasare. S.B. Chinese Journal of Physics. (2011), **49**, No.5, 1070.

## Appendix:



Note: [Y=  $\beta P/\rho$  ,X = $\eta$ ].

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