

## Perturbation approach for equation of state for hard-sphere and Lennard–Jones pure fluids

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MS received 29 October 2010; accepted 29 December 2010

**Abstract.** In this paper we have established the equation of state (EOS) for liquids. The EOS was established for hard-sphere (HS) fluid along with Lennard–Jones (LJ) fluid incorporating perturbation techniques. The calculations are based on suitable axiomatic functional forms for surface tension  $S_m(r)$ ,  $r \geq d/2$  with intermolecular separation  $r$ , as a variable, and  $m$  is an arbitrary real number (pole). The results for  $\beta P/\rho$  from the present EOS thus obtained are compared with Percus-Yevick (PY), scaled particle theory (SPT), and Carnahan–Starling (CS). In addition, we have found a simple EOS for the HS fluid in the region which represents the simulation data accurately.

It is observed that, this EOS for HS gives, PY (pressure) for  $m = 0$ , CS for  $m = 4/5$ , whereas for  $m = 1$  it corresponds to SPT.

**Keywords.** Equation of state (EOS); LJ fluid; HS fluid; computer simulation.

**PACS Nos** 05.70.Ce; 51.30.+i

### 1. Introduction

If all that is needed from a theory for liquids is the equation of state and a prediction of the thermodynamic properties, the equation of state for hard sphere can be given as

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

This equation can be applied to the real fluid if the hard sphere diameter  $d$  is temperature- and density-dependent. Merit of the present approach is its relative conceptual and mathematical simplicity and the information provided about the surface tension of the fluid. Many perturbation and variational theories draw on hard sphere as a reference system. Structural as well as bulk properties of the liquids can be understood by apt approximations. The structure is mainly determined by repulsive forces, whereas the attractive forces merely provide a background potential through which the molecules move. Hard spheres have been dealt with extensively by liquid state theories [1,2]. In two-parameter ( $d$  and  $\epsilon$  which are related to molecular diameter and binding energy of the molecules) perturbation

and variational theories, at higher temperatures repulsive part is dominant whereas at lower temperatures attractive part plays the vital role.

To predict the thermodynamic properties, radial distribution function (RDF) should be developed using intermolecular pair potential. Only contact values appear explicitly, rather than the complete RDF in EOS. Therefore, understanding the contact values of the RDF denoted by  $g(d)$  in hard core fluid, and  $g(d, \epsilon)$  for LJ fluid is sufficient to obtain the EOS. Here  $d$  is the distance of separation at contact between the centres of two interacting fluid particles. The thermodynamic and structural properties of the realistic model can be obtained using more precise and well-defined probability distribution function [3,4] in a perturbation theory. Here, we assume surface tension as some arbitrary function of the cavity with radius  $r = d$  and  $\epsilon$  as the binding energy.

The present work is organized as follows: Section 2.1 deals with the computation of the work done for  $r \leq d/2$ . Section 2.2 deals with work done for  $r \geq d/2$ . In §2.3 evaluation of constants  $A$  and  $B$  is carried out as also the equation of state has been derived using boundary conditions. Results are discussed in §3. Section 4 gives conclusion.

## 2. Formulation of work done

Consider the formation of a cavity of radius  $r$  in a hard-sphere fluid. Let  $\rho G(r, \rho)$  be the concentration of the centres of the spheres on the surface of the cavity. The cavity plays exactly the role of another hard sphere of diameter  $(2r - d)$ , as it excludes the centres of other particles from the spherical region. The function  $G(r)$  can be calculated using 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 centre of the cavity. The probability that a cavity of radius  $r < d/2$  is empty is  $p(r) = 1 - (4/3)\pi r^3 \rho$ , as one particle, at the most, may be located there.

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

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

The above two expressions lead to

$$G(r) = (1 - (4/3)\pi r^3 \rho)^{-1}; \quad r < d/2.$$

### 2.1 Probability function approach (PFA) for work done and radial distribution function $g(r)$ in a pure liquid for $r \leq d/2$

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

$$p(v) = v\rho, \quad \rho = N/V$$

and probability of the cavity being empty is  $[1 - p(v)]$ .

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

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

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In this equation the interaction pair potential  $u(r)$  can be treated as hard-sphere potential  $u_{\text{HS}}$  if  $r < d$ , and  $u(r)$  can be treated as  $u_{\text{LJ}}$  potential if  $r \geq d$ . Therefore, we have

$$\begin{aligned} u(r) &= u_{\text{HS}}, \quad r < d; \\ u(r) &= u_1(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad \sigma = \alpha d, \quad r \geq d \end{aligned} \quad (2)$$

as the interaction pair potential,  $\epsilon$  is the depth of LJ potential,  $\alpha$  relates HS parameter  $d$  to the corresponding LJ parameter  $\sigma$ . With the help of hard-sphere potential, we define the heaviside function as follows:

$$\begin{aligned} \exp[-\beta u_{\text{HS}}] &= \text{Heaviside}(r - d); \\ \text{Heaviside}(r - d) &= 0, \quad r < d; \quad \text{Heaviside}(r - d) = 1, \quad r \geq d. \end{aligned} \quad (3)$$

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

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

where  $p_0(d)$  is related to hard-sphere parameter  $d$ , and [ $p_1(d), p_2(d)$ ] are related to the variables  $\epsilon$  and  $d$ .

$$\begin{aligned} p_0(d) &= \left[ 1 - \frac{d^3 N}{R^3} \right], \quad p_1(d) = \left[ \frac{f_1 \beta \epsilon d^3 N}{R^3} \right], \quad p_2(d) = \left[ \frac{f_2 \beta^2 \epsilon^2 d^3 N}{R^3} \right], \\ f_1(\alpha) &= -3 \left[ \frac{4}{9} \alpha^{12} - \frac{4}{3} \alpha^6 \right], \quad f_2(\alpha) = \frac{3}{2} \left[ \frac{16}{21} \alpha^{24} - \frac{32}{15} \alpha^{18} + \frac{16}{9} \alpha^{12} \right], \\ f(\beta\epsilon) &= 1 - f_1 \beta \epsilon - f_2 \beta^2 \epsilon^2. \end{aligned}$$

For hard sphere,  $p_0(r)$  is the probability [2] that a cavity is empty. General expression for probability  $p(r)$  can now be as follows:

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

The probability that a spherical shell contains a molecule can be represented as

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

where

$$\begin{aligned} p_0(r) &= \left[ 1 - \frac{r^3 N}{R^3} \right] = \left[ 1 - \frac{(4\pi r^3/3)N}{V} \right], \quad p_1(r) = \left[ \frac{f_1 \beta \epsilon r^3 N}{R^3} \right], \\ p_2(r) &= \left[ \frac{f_2 \beta^2 \epsilon^2 r^3 N}{R^3} \right]. \end{aligned}$$

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

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

where

$$p_0(r) = \left[ 1 - \frac{8\eta r^3}{d^3} \right], \quad p_1(r) = \left[ \frac{8\eta f_1 \beta \epsilon r^3}{d^3} \right], \quad p_2(r) = \left[ \frac{8\eta f_2 \beta^2 \epsilon^2 r^3}{d^3} \right].$$

The relation [5]

$$\beta W(r) = -\ln[p(r)], \quad r \leq d/2 \tag{6}$$

gives the reversible work  $W(r)$  necessary for creating a cavity of radius  $r$  in the real fluid.  $p(r)$ ,  $W$  and  $G$  depend exclusively on  $(r, \eta, \epsilon)$ .  $W(r)$  is obtained by removing higher-order terms  $O(\eta^2)$ , and split into two parts as follows:

$$\beta W = \beta W_0 + [\beta W_1 + \beta W_2], \quad r \leq d/2. \tag{7}$$

$$\beta W_0 = -\ln \left[ 1 - \frac{8\eta r^3}{d^3} \right], \quad \beta W_1 = \left[ \frac{8\eta f_1 \beta \epsilon r^3}{d^3} \right], \quad \beta W_2 = \left[ \frac{8\eta f_2 \beta^2 \epsilon^2 r^3}{R^3} \right].$$

$W_0$  corresponds to hard-sphere interaction potential, whereas  $[W_1, W_2]$  relates to perturbing LJ potential part. Expression for  $[(dW_0/dr), (dW_1/dr), (dW_2/dr)]$  can be written as

$$\beta \frac{dW_0}{dr} = \frac{24\eta r^2}{d^3 \left[ 1 - \frac{8\eta r^3}{d^3} \right]}, \quad \beta \frac{dW_1}{dr} = \left[ \frac{24\eta f_1 \beta \epsilon r^2}{d^3} \right],$$

$$\beta \frac{dW_2}{dr} = \left[ \frac{24\eta f_2 \beta^2 \epsilon^2 r^2}{d^3} \right].$$

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

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

Now we can express  $G(r)$  as

$$G(r) = \frac{\beta}{\rho} \left[ \frac{dW}{dV} \right] = \frac{1}{\left[ 1 - \frac{8\eta r^3}{d^3} \right]} + \beta \epsilon f_1 + \beta^2 \epsilon^2 f_2, \quad r \leq d/2. \tag{9}$$

### 2.2 Thermodynamic function approach (TFA) for work done and radial distribution function $G(r)$ for $r \geq d/2$

Work done is stated as

$$dW(r) = P dV - S dA = k_B T \rho G(r) dV. \tag{10}$$

Here  $dA$  and  $dV$  are the increase in surface area and volume respectively. For a real fluid, hard-sphere potential along with perturbing potential LJ contribute effective net positive value for surface tension  $S$ .

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

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

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But the equation of state for a fluid in terms of hard-sphere diameter  $d$  and binding energy  $\epsilon$  is expressed [2] as

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

Thermodynamic properties can be obtained by requiring that radial distribution function is to be continuous at a contact point. Hence we can write  $g_{(\text{PFA})}(d) = G_{(\text{TFA})}(d)$

$$g(d) = G(d) \quad (13)$$

and we say that empty sphere of radius  $d$  affects the remainder of the fluid precisely like another molecule. Thus, eq. (11) can be written as

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

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 [6] the following expression:

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

where  $A$  and  $B$  are constants to be determined. Surface tension, suggested by Kirkwood and Buff [7] can be obtained for  $m = 1$  as

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

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

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

On substitution of  $S_m(r)$ , we get the corresponding  $G_m(r)$  as given below:

$$G_m(r) = \frac{\beta P}{\rho} - \frac{d}{r} A + \left[ -m \frac{r}{d} + 1 + m \right] B, \quad r \geq d/2.$$

### 2.3 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  $G(r)$  as

$$G(r) = \frac{1}{\left[ 1 - \frac{8\eta r^3}{d^3} \right]} + \beta\epsilon f_1 + \beta^2\epsilon^2 f_2, \quad r \leq d/2.$$

We also have the following expressions for  $G(r)$ :

$$G(r) = G_m(r) = -\frac{1}{(-1 + 4\eta)} + \left[ \frac{4\eta}{(-1 + 4\eta)} - \frac{d}{r} \right] A + \left[ -m \frac{r}{d} + 1 + m - \frac{4\eta}{(-1 + 4\eta)} \right] B, \quad r \geq d/2.$$

The values for  $A$  and  $B$  are worked out as follows:

$$A = A_{\text{sol}}(0)_m + A_{\text{sol}}(1)_m, \quad B = B_{\text{sol}}(0)_m + B_{\text{sol}}(1)_m, \quad (18)$$

where

$$A_{\text{sol}}(0)_m = \frac{(3/4)\eta(-2 + 3m\eta)}{(\eta - 1)^2(m\eta - 1)};$$

$$A_{\text{sol}}(1)_m = \frac{(1/3)(-3 + \alpha^6)(-1 + 4\eta)\beta\epsilon\alpha^6 m}{(m\eta - 1)};$$

$$B_{\text{sol}}(0)_m = \frac{3\eta^2}{(\eta - 1)^2(m\eta - 1)};$$

$$B_{\text{sol}}(1)_m = \frac{(4/3)\alpha^6\beta\epsilon(-3 + \alpha^6)(-1 + 4\eta)}{(m\eta - 1)}$$

0 represents reference potential and 1 is used for the perturbing LJ potential. Equation of state for the model fluid can now be stated as

$$\beta P/\rho = Z(\text{SBK}) = eq(0)_m + eq(1)_m. \quad (19)$$

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

$$eq(0)_m = \frac{[1 + (2 - m)\eta + (3 - 2m)\eta^2]}{(1 - \eta)^2(1 - m\eta)};$$

$$eq(1)_m = \frac{(f_1\beta\epsilon + f_2\beta^2\epsilon^2)(m - 4)\eta}{(1 - m\eta)}. \quad (20)$$

### 3. 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).

$Z1 = Z(\text{SBK})_{m=3/4}$ ,  $Z2 = Z(\text{CS})$ ,  $Z3 = Z(\text{SPT})_{m=1}$ ,  $Z4 = Z(\text{PY}(P))_{m=0}$ ,  $Z5 = Z(\text{SBK})_{m=4/5}$  denote different EOS in table 1 and  $Z1 = Z(\text{SBK})_{m=3/4}$ ,  $Z2 = Z(\text{BH2})$ , denote different EOS in table 2.

#### 3.1 Case A: Hard-sphere potential

Comparative study of table 1 suggests that EOS presented gives values of  $Z$  well in agreement with  $Z(\text{MD})$ .

$$Z1(\text{SBK}) = eq(0)_{3/4} = \frac{[4 + 5\eta + 6\eta^2]}{(1 - \eta)^2(4 - 3\eta)}. \quad (21)$$

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**Table 1.** Different equations of state (EOS) for hard-sphere potential.

$\eta$	Z(MD)	Z1(SBK)	Z2(CS)	Z3(SPT)	Z4(PY)	Z5(SBK)
0.052	1.24	1.24	1.24	1.24	1.24	1.24
0.105	1.55	1.55	1.55	1.55	1.55	1.55
0.157	1.96	1.97	1.97	1.97	1.95	1.97
0.209	2.52	2.52	2.52	2.54	2.48	2.52
0.262	3.27	3.27	3.26	3.31	3.17	3.27
0.314	4.29	4.29	4.28	4.38	4.09	4.30
0.367	5.71	5.70	5.71	5.90	5.32	5.74
0.419	7.73	7.71	7.75	8.12	7.00	7.74
0.471	10.70	10.63	10.75	11.45	9.33	10.77
0.524	15.00	14.99	15.30	16.63	12.64	15.26

For  $m = 1$ , we have Percus–Yevick PY(compressibility) = Z(SPT) as

$$Z3(SPT) = eq(0)_1 = \frac{[1 + \eta + \eta^2]}{(1 - \eta)^3}. \quad (22)$$

For  $m = 0$ , we have Percus–Yevick PY(pressure) = Z(PY) as

$$Z4(PY) = eq(0)_0 = \frac{[1 + 2\eta + 3\eta^2]}{(1 - \eta)^2}. \quad (23)$$

And for  $m = 4/5$ , results numerically close to Carnahan–Starling = Z(CS),

$$Z2(CS) \approx Z5(SBK) = eq(0)_{4/5}, \quad (24)$$

$$Z2(CS) = \frac{[1 + \eta + \eta^2 - \eta^3]}{(1 - \eta)^3}; \quad eq(0)_{4/5} = \frac{[5 + 6\eta + 7\eta^2]}{(1 - \eta)^2(5 - 4\eta)}. \quad (25)$$

**Table 2.** Different equations of state (EOS) for Lennard–Jones fluid at critical temperature.

$\eta$	Z(MD)	Z1(SBK)	Z2(BH2)
0.052	0.72	0.75	0.74
0.105	0.50	0.54	0.52
0.157	0.35	0.38	0.36
0.209	0.27	0.30	0.26
0.262	0.30	0.35	0.27
0.288	0.41	0.45	0.35
0.340	0.80	0.85	0.74
0.393	1.73	1.64	1.64
0.445	3.37	3.06	3.36
0.497	6.32	5.49	6.32

### 3.2 Case B: Lennard–Jones (LJ) potential

The comparison (table 2) shows the closeness of values of  $Z$  with molecular dynamics  $Z(\text{MD})$  results.

For  $m = 3/4$  and  $\alpha = 3^{(1/6)}$  we have the following results for equation of state ( $\beta P/\rho$ ):

$$(\beta P/\rho) = Z(\text{SBK}) = eq(0)_{3/4} + eq(1)_{3/4}, \quad (26)$$

$$eq(0)_{3/4} = \frac{[4 + 5\eta + 6\eta^2]}{(1 - \eta)^2(4 - 3\eta)}; \quad eq(1)_{3/4} = -\frac{(3432/35)\beta^2\epsilon^2\eta}{[1 - \frac{3}{4}\eta]} \quad (27)$$

with critical constants  $\eta_c = 0.1572541882$ ,  $(\beta\epsilon)_c = 0.30189835348$  (functional form dependent!).

## 4. Conclusion

It is thus seen that, we have the same mathematical result, for physical property such as compressibility factor  $(\beta P/\rho) = Z(\text{SBK})$ , which corresponds to the present axiomatic form. For the entire density region there is a close agreement with  $Z(\text{MD})$  results with  $m = 3/4$  in hard-sphere formulation, while  $Z(\text{LJ})$  values of the present formulation deviate from  $Z(\text{MD})$  in high-density region.

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