A comprehensive approach to an equation of state for hard spheres and Lennard–Jones fluids

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We present a simple method of obtaining various equations of state for hard sphere fluid in a simple unifying way. We will guess equations of state by using suitable axiomatic functional forms ($n = 1, 2, 3, 4, 5$) for surface tension $S_m^n(r)$, $r \geq d/2$ with intermolecular separation r as a variable, where m is an arbitrary real number (pole). Among the equations of state obtained in this way are Percus–Yevick, scaled particle theory and Carnahan–Starling equations of state. In addition, we have found a simple equation of state for the hard sphere fluid in the region that represents the simulation data accurately. It is found that for both hard sphere fluids as well as Lennard–Jones fluids, with $m = 3/4$ the derived equation of state (EOS) gives results which are in good agreement with computer simulation results. Furthermore, this equation of state gives the Percus–Yevick (pressure) EOS for the $m = 0$, the Carnahan–Starling EOS for $m = 4/5$, while for the value of $m = 1$ it corresponds to a scaled particle theory EOS.

Keywords: equation of state, Lennard–Jones potential, hard-sphere potential, computer algebra, computer simulation

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1. Introduction

Scaled particle theory has been well established for several decades and the equations of state (EOS) of hard sphere and Lennard–Jones fluids are well documented. The present work attempts to bring a new contribution to a well-investigated subject. The conceptualization of a hard sphere is very useful for the improvement of theories of the liquid state. With suitable computation, results for the bulk and structural properties of liquids can be obtained with ease. The hard sphere system can be used as a reference system for many perturbation and variation theories.[1−7] The fundamental nature of two parameters is related to the molecular diameter σ and the binding energy of the molecule ϵ. In perturbation and variation theories, at high temperatures only the repulsive part of the potential is prominent, while at lower temperatures the attractive part becomes prominent. The use of a precise and well-defined probability distribution function[8−11] in perturbation theory opens up the possibility of deriving a closed theoretical scheme for the determination of thermodynamic and structural properties in a more realistic model. Robles and de Haro[12] used CS as a reference system. Wu and Sadus[13] conducted comparative studies of EOS for hard spheres. The author in Ref. [14] used the strong repulsive potential together with a weak short-range attractive potential. The current approach assumes that the thermodynamic property is the surface tension, as some impulsive function of intermolecular distance r, hard sphere diameter d and ϵ as binding energy.

The rest of this paper is organized as follows. In Subsection 2.1 a new functional approach is used for the computation of the probability distribution function and related work is done. Subsection 2.2 deals with the thermodynamic work done. The equation of state and the expression for the surface tension are derived using boundary conditions in Subsection 2.3. Section 3 is devoted to its application to a real fluid system and discussion. Section 4 gives the conclusion.

2. Formulation

2.1. Functional approach

Let $p(d)$ be the probability that there is no pair-molecule, whose centre lies within a sphere of radius d, centred about some specified point

$$p(d) = \frac{\int_0^R \mathrm{e}^{-\beta u(r)} 4\pi r^2 \mathrm{d}r}{\int_0^R 4\pi r^2 \mathrm{d}r}, \quad r \leq d,$$

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$$R = \left[\frac{3V}{4\pi}\right]^{1/3}, \quad \beta = \frac{1}{K_{\rm B}T}. \tag{1}$$

In the above equation, $u(r)$

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

is the interaction pair-potential, α is an arbitrary parameter and V is the volume of the system. With the help of the hard sphere potential, we define the following Heaviside function

$$\exp\left[-\beta u_{\rm HS}\right] = \text{Heaviside}\left(r - d\right). \tag{3}$$

Now $p(d)$ is evaluated and suitably approximated. This probability $p(d)$ is expressed correspondingly as the sum of two parts, $p_0(d)$ is the hard sphere potential, $p_1(d)$ and $p_2(d)$ are the remaining potential parts, i.e.

$$p(d) = p_0(d) + \left[p_1(d) + p_2(d)\right],$$

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

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

So it is easy to assume[7] the first term $p_0(r)$ as the probability of the absence of a single molecule. For the Lennard–Jones (LJ) potential, $p(r)$ is again expressed as a sum of two parts

$$p(r) = p_0(r) + \left[p_1(r) + p_2(r)\right], \quad r \leq d/2, \tag{4}$$

where

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

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

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

$$p_2(r) = \left[\frac{8\eta f_2\beta^2\epsilon^2 r^3}{d^3}\right], \tag{5}$$

where N is the Avogadro number.

Now $-\mathrm{d}p_0$ is the probability of finding an empty sphere, whose radius lies between r and $r + \mathrm{d}r$. So we say that $-\mathrm{d}p$ is the probability of finding an empty sphere whose radius lies between r and $r + \mathrm{d}r$. This is equal to the product of the probability $p(r)$ of having no molecule within the radius r and conditional probability $G(r)(4\pi r^2\mathrm{d}r)$ of there being a centre of at least one molecule, within $\mathrm{d}r$ of r, when no molecule is inside the sphere of radius r. Thus

$$-\left[\frac{\mathrm{d}p(r)}{\mathrm{d}r}\right] = p(r)4\pi\rho r^2 G(r), \quad r \leq d/2. \tag{6}$$

The relation[6]

$$\beta W(r) = -\ln\left[p(r)\right], \quad r \leq d/2, \tag{7}$$

gives the reversible work $W(r)$ necessary to create a cavity of radius r in the real fluid. It should be noted that $p(r)$, W and G depend upon (r, η, ϵ). This $W(r)$ is approximated and split into two parts for easy interpretation

$$\beta W \approx \beta W_0 + \left[\beta W_1 + \beta W_2\right], \quad r \leq d/2, \tag{8}$$

where

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

W_0 corresponds to the hard sphere interaction potential part, and $[W_1, W_2]$ is the work done due to the perturbing LJ potential part. The expression for $[(\mathrm{d}W_0/\mathrm{d}r), (\mathrm{d}W_1/\mathrm{d}r), (\mathrm{d}W_2/\mathrm{d}r)]$ can be written as

$$\begin{aligned} \beta\frac{\mathrm{d}W_0}{\mathrm{d}r} &= \frac{24\eta r^2}{d^3\left[1 - 8\eta r^3/d^3\right]}, \\ \beta\frac{\mathrm{d}W_1}{\mathrm{d}r} &= \left[\frac{24\eta f_1\beta\epsilon r^2}{d^3}\right], \\ \beta\frac{\mathrm{d}W_2}{\mathrm{d}r} &= \left[\frac{24\eta f_2\beta\epsilon r^2}{d^3}\right]. \end{aligned}$$

Normally $W(r)$ is related to the thermodynamic work done against the external force (pressure) and internal force (surface tension). Combining the above two equations, the following expression can be obtained

$$\frac{\mathrm{d}p_0}{p_0} = -\beta\mathrm{d}W = -4\pi\rho G(r) r^2\mathrm{d}r, \quad r \leq d/2. \tag{9}$$

So that we have expression for $G(r)$ as

$$\frac{\beta}{\rho}\left[\frac{\mathrm{d}W}{\mathrm{d}V}\right] = G(r) = \frac{1}{\left[1 - 8\eta r^3/d^3\right]} - \beta\epsilon f_1 - \beta^2\epsilon^2 f_2, \quad r \leq d/2. \tag{10}$$

2.2. Thermodynamic approach

The general work done is stated in terms of surface area $\mathrm{d}A$ and volume of the system $\mathrm{d}V$

$$\mathrm{d}W(r) = P\mathrm{d}V - S\mathrm{d}A = K_{\mathrm{B}}T\rho G(r)\mathrm{d}V. \quad (11)$$

For a real fluid, the reference potential (hard sphere) along with the perturbing potential (LJ) contribute an effective net positive value for surface tension S. Hence $P\mathrm{d}V$ and $S\mathrm{d}A$ must have an opposite sign. This leads to the correct sign prediction for surface tension.

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

$$G(r) = \frac{[P - 2S/r]}{\rho K_{\mathrm{B}}T}. \quad (12)$$

However, an equation of state for a fluid in terms of hard sphere diameter d and binding energy ϵ is expressed as

$$\frac{\beta P}{\rho} = [1 + 4\eta\ g(d)]\,. \quad (13)$$

The factor $\pi d^3/6$ and ρ represents, volume of sphere and number density respectively. Pressure can be estimated by finding $g(d)$, the radial distribution function, for spheres at contact. As $G(r)$ is used, because an empty sphere of radius d affects the remainder of the fluid precisely like another molecule, i.e.

$$g(d) = G(d). \quad (14)$$

On combining, we obtain an equation as

$$\frac{\beta P}{\rho} = [1 + 4\eta\ G(d)]\,. \quad (15)$$

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. It is reasonable to assume[9] an expression of the following type

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

where A and B are suitable constants to be determined. Hence we simply draw the conclusion that, at a molecular level, surface tension varies in accordance with the radius of curvature. This is also the central approximation of scaled particle theory (SPT) which is used for $r \geq d/2$ and reduces to old[7] exact form. Gibbs surface tension, suggested by Kirkwood and Buff[10] can be obtained for $m = 1$ as

$$S(r) = S_0\left[1 + 2\delta\left(\frac{d}{r}\right)\right], \quad r \geq d/2, \quad (17)$$

see Scaled Particle Theory, page 618 Eq. (5.8)) *Rev. Mod. Phys.* **48** (1976).

In the present paper, we study $f(r)$ extensively, with a view to obtain simpler functional forms of EOS, providing numerical results close to earlier ones. To achieve such a target we assume the following new functional form for thermodynamic approach, as given below

$$S(r) = S_m^n(r) = [A + Bf(r)]\,, \quad r \geq d/2, \quad n = 1, 2, 3, 4, 5, \quad (18)$$

where $S_m^n(r)$ are shown in Appendix A. Substituting the generalized functional form for $S_m^n(r)$, we obtain the corresponding $G_m^n(r)$ given in Appendix B.

2.3. Condition of continuity

Using the SPT, we obtain an expression for $G(r)$

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

and from the thermodynamic approach we have the following expressions for $G(r)$

$$G(r) = G_m^n(r), \quad n = 1, 2, 3, 4, 5,$$

where $G_m^n(r)$ are shown in Appendix C.

The resulting values for A and B are computed by imposing the condition of continuity [$G(r)$ and $\mathrm{d}G(r)/\mathrm{d}r$] at $r = d/2$ (contact point). Thus we have the following corresponding solutions, as follows:

$$A = A\,\mathrm{sol}(0)_m^n + A\,\mathrm{sol}(1)_m^n,$$
$$B = B\,\mathrm{sol}(0)_m^n + B\,\mathrm{sol}(1)_m^n; \quad n = 1, 2, 3, 4, 5, \quad (19)$$

and it is shown in Appendix D, where zero and one are used for the reference potential and a LJ perturbed term, respectively. Hence, using different assumptions, we have a corresponding set of EOSs and $S_m^n(d)$. The general equation of state for the model fluid becomes

$$\frac{\beta P}{\rho} = Z_m^n = \mathrm{eq}(0)_m^n + \mathrm{eq}(1)_m^n, \quad n = 1, 2, 3, 4, 5, \quad (20)$$

where

$$\mathrm{eq}(0)_m^n = \frac{\left[1 + (2-m)\eta + (3-2m)\eta^2\right]}{(1-\eta)^2(1-m\eta)},$$
$$\mathrm{eq}(1)_m^n = \frac{(f_1\beta\epsilon + f_2\beta^2\epsilon^2)(m-4)\eta}{(1-m\eta)}, \quad n = 1, 2, 3, 4,$$

and

$$\mathrm{eq}(0)_m^5 = \frac{\left[a_0 + a_1\eta + a_2\eta^2\right]}{(1-\eta)^2(b_0 - b_1\eta)},$$

with a_0, a_1, a_2, b_0, and b_1 shown in Appendix E.

$$\mathrm{eq}(1)_m^5 = \frac{\eta\exp[\frac{2}{5}\beta\epsilon](f_1\beta\epsilon + f_2\beta^2\epsilon^2)(35m - 140 + 6\beta\epsilon m - 12\beta\epsilon)}{\left[35\eta\exp[-\frac{2}{5}\beta\epsilon]m + 140\eta - 140\eta\exp[-\frac{2}{5}\beta\epsilon] + 6\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon]m - 12\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon] - 35\right]}.$$

2.4. Special case: $\alpha^6 = 3$

We have useful relation $\sigma = \alpha d$, between hard sphere potential and LJ potential. Selecting $\alpha^6 = 3$ gives $A\,\mathrm{sol}(1)_m^n = 0$, $B\,\mathrm{sol}(1)_m^n = 0$. It is observed that α is directly related to surface tension. Here, we assume that at a critical point, surface tension persists due to hard sphere potential only. This hard sphere potential is directly related to hard convex molecular geometry, which is not affected at any temperature range. We define the following physical quantity related to surface tension $S(d)$ in an assumed form

$$\begin{aligned}&\text{surface tension (reduced)} = \beta S\,(r = d)\,(\pi d^2/4),\\ &\sigma = \alpha d, \end{aligned} \tag{21}$$

Normally, such a construction is expected to be good, because the first term is arbitrarily added with a derived perturb term. It is observed from the following equation that different forms of $f(r/d, A, B)$ yield different EOS in the present formulation

$$\begin{aligned} S_m^n(d) &= S = (d/2)(\rho/\beta)f(r/d, A, B)\\ &= \frac{(9/16)\eta^2(2 + 4\eta - 3m\eta)}{(1-\eta)^2(1-m\eta)\beta},\\ &\quad n = 1, 2, 3, 4, 5. \end{aligned} \tag{22}$$

In the following equation we have different A and B but the same EOS

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

$$\mathrm{eq}(1)_m^n = \frac{(1056/35)(m-4)\beta^2\epsilon^2\eta}{(1-m\eta)}, \quad n = 1, 2, 3, 4,$$

and

$$\mathrm{eq}(0)_m^5 = -\frac{[a_2\eta^2 + a_1\eta + a_0]}{(1-\eta)^2(b_1\eta - b_0)},$$

$$\mathrm{eq}(1)_m^5 = -\frac{(1056/35)(-140 + 35m + 6\beta\epsilon m - 12\beta\epsilon)\exp[-\frac{2}{35}\beta\epsilon]\eta\beta^2\epsilon^2}{(140\eta - 140\eta\exp[-\frac{2}{35}\beta\epsilon] + 35\eta\exp[-\frac{2}{35}\beta\epsilon]m + 6\beta\epsilon\eta\exp[-\frac{2}{35}\beta\epsilon]m - 12\beta\epsilon\eta\exp[-\frac{2}{35}\beta\epsilon] - 35)}.$$

For $\alpha = 3^{(1/6)}$ we obtain, for critical constants, a conjugate root $(\eta_c, \pm\beta\epsilon_c)$. For $\alpha = 3^{(1/6)}$ we show that the surface tension due to hard sphere potential still persists and contributes because of the perturbing LJ potential vanishing. This seems to be quite a close approximation of a real fluid. If $\alpha \neq 3^{(1/6)}$ then we have two roots $(\eta_c, \beta\epsilon_{c1})$ and $(\eta_c, -\beta\epsilon_{c2})$ for $0 \leq \eta_c \leq 1.0$ and the relation between these two roots is given by the following equation

$$\beta\epsilon_{c1} + \beta\epsilon_{c1} = \beta\epsilon_0 = \frac{(35/2)\alpha^6 - 3}{\alpha^6\,[15\alpha^{12} - 42\alpha^6 + 35]}. \tag{23}$$

We denote the origin of the surface tension for a real fluid as the sum of surface tensions due to hard sphere potential and perturbing LJ potential. By imposing the additional condition on α, the surface tension at a critical temperature due to the perturbing LJ potential vanishes

$$A\,\mathrm{sol}(1)_m^n = 0, \quad B\,\mathrm{sol}(1)_m^n = 0. \tag{24}$$

So at critical temperature, if $\alpha^6 = 3$ then $A\,\mathrm{sol}(1)_m = 0$, $B\,\mathrm{sol}(1)_m = 0$. This shows that α is directly related to surface tension due to the hard sphere.

3. Application to a real fluid system and discussion

3.1. Case A: hard sphere potential with different values of m and $\alpha = 0$

For a high temperature limit we have $\beta\epsilon = 0$. The illustration in Table 1 suggests that the present proposed EOS is in agreement with the Z molecular dynamics (MD) result.

We expect that if the surface tension for a real fluid is positive, then the reference term (hard sphere potential) should be sufficiently large as compared to the perturbing LJ potential term.

$$Z(\mathrm{ESPT}) = \mathrm{eq}(0)_{3/4}^n = \frac{\left[4 + 5\eta + 6\eta^2\right]}{(1-\eta)^2(4-3\eta)}.$$

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

$$Z(\mathrm{SPT}) = \mathrm{eq}(0)_1^n = \frac{\left[1 + \eta + \eta^2\right]}{(1-\eta)^3}.$$

For $m = 0$, it yields Percus–Yevick PY (pressure)=Z(PY) as

$$Z(\mathrm{PY}) = \mathrm{eq}(0)_0^n = \frac{\left[1+2\eta+3\eta^2\right]}{(1-\eta)^2}.$$

In addition $m = 4/5$ is numerically close to Carnahan Starling=Z(CS) as

$$Z(\mathrm{CS}) = \mathrm{eq}(0)_{4/5}^n = \frac{\left[5+6\eta+7\eta^2\right]}{(1-\eta)^2(5-4\eta)} \approx \frac{\left[1+\eta+\eta^2-\eta^3\right]}{(1-\eta)^3}.$$

Let

$$Z_1 = Z(\mathrm{ESPT})_{m=3/4}, \quad Z_2 = Z(\mathrm{CS}),$$
$$Z_3 = Z(\mathrm{SPT})_{m=1}, \quad Z_4 = Z(\mathrm{PY}(P))_{m=0},$$

and $Z_5 = Z(\mathrm{ESPT})_{m=4/5}$ be denoting different EOS in the following Table 1.

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

S. No	η	Z(MD)	Z_1	Z_2	Z_3	Z_4	Z_5
1	0.052	1.24	1.24	1.24	1.24	1.24	1.24
2	0.105	1.55	1.55	1.55	1.55	1.55	1.55
3	0.157	1.96	1.97	1.97	1.97	1.95	1.97
4	0.209	2.52	2.52	2.52	2.54	2.48	2.52
5	0.262	3.27	3.27	3.26	3.31	3.17	3.27
6	0.314	4.29	4.29	4.28	4.38	4.09	4.30
7	0.367	5.71	5.70	5.71	5.90	5.32	5.74
8	0.419	7.73	7.71	7.75	8.12	7.00	7.74
9	0.471	10.70	10.63	10.75	11.45	9.33	10.77
10	0.524	15.00	14.99	15.30	16.63	12.64	15.26

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

This occurs with different values of m and $\alpha = 3^{(1/6)}$, i.e. at a critical temperature. The algorithm used in deriving the present EOS gives the highest accuracy for the hard sphere part of fluid. The computed results are better than Barker and Henderson's first order perturbation approach, while inferior to the second order perturbation approach at a higher density region. For a better numerical agreement with the molecular dynamics Z(MD) result, the algorithm needs to be confined with the termination of the higher terms in the probability expression $p(r)$.

For both choices of critical constants, it has been observed that the selection of α does not affect the Z(ESPT). For $m = 3/4$, $\alpha = 3^{(1/6)}$ and $n = 1, 2, 3, 4$ we have the following new result for the equation of state ($\beta P/\rho$)

$$(\beta P/\rho) = Z(\mathrm{ESPT}) = \mathrm{eq}(0)_{3/4}^n + \mathrm{eq}(1)_{3/4}^n,$$
$$\mathrm{eq}(0)_{3/4}^n = \frac{\left[4+5\eta+6\eta^2\right]}{(1-\eta)^2(4-3\eta)},$$
$$\mathrm{eq}(1)_{3/4}^n = -\frac{(3432/35)\beta^2\epsilon^2\eta}{\left[1-\frac{3}{4}\eta\right]}$$

with critical constants

$$\eta_\mathrm{c} = 0.1572541882, \quad \epsilon_\mathrm{c} = \pm 0.30189835348. \quad (25)$$

Let

$$Z_1 = Z(\mathrm{ESPT})_{m=3/4}^n, \quad Z_2 = Z(\mathrm{BH2}),$$
$$Z_3 = Z(\mathrm{SPT})_{m=1}^n, \quad Z_4 = Z(\mathrm{PY(P)})_{m=0}^n,$$

$Z_5 = Z(\mathrm{ESPT})_{m=4/5}$, and for corresponding to $S(r) = S_{4/5}^5(r)$, $Z_6 = Z(\mathrm{ESPT})_{m=3/4}^5$, be denoting different EOS. See Table 2.

Table 2. Different equation of state (EOS) for Lennard–Jones fluid.

S. No	η	Z(MD)	Z_1	Z_2	Z_3	Z_4	Z_5	Z_6
1	0.052	0.72	0.75	0.74	0.78	0.69	0.76	0.77
2	0.105	0.50	0.54	0.52	0.57	0.45	0.54	0.57
3	0.157	0.35	0.38	0.36	0.41	0.31	0.38	0.41
4	0.209	0.27	0.30	0.26	0.32	0.29	0.30	0.32
5	0.262	0.30	0.35	0.27	0.34	0.43	0.35	0.35
6	0.288	0.41	0.45	0.35	0.41	0.58	0.44	0.44
7	0.340	0.80	0.85	0.74	0.75	1.09	0.83	0.83
8	0.393	1.73	1.64	1.64	1.49	1.98	1.62	1.68
9	0.445	3.37	3.06	3.36	2.90	3.40	3.03	3.31
10	0.497	6.32	5.49	6.32	5.49	5.62	5.49	6.31

For $m = 1$, we have the following Reiss *et al.*[8] and Percus Yevick (compressibility) results,

$$Z(\mathrm{SPT}) = \mathrm{eq}(0)_1^n + \mathrm{eq}(1)_1^n, \quad \mathrm{eq}(0)_1^n = \frac{\left[1+\eta+\eta^2\right]}{(1-\eta)^3},$$
$$\mathrm{eq}(1)_1^n = \frac{(6336/35)\beta^2\epsilon^2\eta}{(2\eta-2)},$$

where the $\mathrm{eq}(1)_1^n$ perturbation term appears as a modification, with critical constants

$$\eta_\mathrm{c} = 0.168254401781, \quad \beta\epsilon_\mathrm{c} = \pm 0.304233443198. \quad (26)$$

For $m = 0$ in the present formulation, which is an extension of SPT, we have the following surface tension result along with Percus Yevick (pressure)

$$Z(\mathrm{PY}) = \mathrm{eq}(0)_0^n + \mathrm{eq}(1)_0^n,$$

$$\text{eq}(0)_0^n = \frac{\left[1+2\eta+3\eta^2\right]}{(1-\eta)^2},$$
$$\text{eq}(1)_0^n = -(4224/35)\beta^2\epsilon^2\eta,$$

where $\text{eq}(1)_0^n$ perturbation term appears as a modification, with critical constants

$$\eta_c = 0.134465524085, \quad \beta\epsilon_c = \pm 0.294703254977. \quad (27)$$

At a critical point, the selection of α does not affect Z(ESPT) but does affect the surface tension.

4. Conclusion

It is thus seen that we have the same mathematical result for a physical property such as the compressibility factor $(\beta P/\rho) = \text{eq}(0)_m^n$, which corresponds to different axiomatic forms $(n = 1, 2, 3, 4, 5)$ for surface tension at a molecular level for HS fluid, while it is numerically close for $n = 1, 2, 3, 4$ for LJ fluid but substantially improved for $n = 5$. There is close agreement with the molecular dynamics results with $m = 3/4$ and $\alpha = 0$ in the above formulation.

Appendix A

The function $S_m^n(r)$ is explicitly given as follows:

$$S_m^1(r) = A + B\left[\frac{m_1}{(d/r)^{-2}} - \frac{(m_1+4)}{(d/r)^{-1}}\right],$$
$$m_1 = \frac{(1-m)}{\left[1-\frac{3}{4}m\right]},$$
$$S_m^2(r) = A + B\left[\frac{m}{(d/r)^{-1}} - 4\frac{(1-m)}{(d/r)^1}\right],$$
$$S_m^3(r) = A + B\left[\frac{m}{(d/r)^2} - \frac{(1+m)}{(d/r)^1}\right],$$
$$S_m^4(r) = A + B\left[1-\frac{d}{r}\right]^{1/(2-m)},$$
$$S_m^5(r) = S_m^1(r) exp\left[-\frac{2}{35}\beta\epsilon\left(\frac{2r}{d}\right)^3\right].$$

Appendix B

Substituting the generalized functional form for $S_m^n(r)$, we obtain the corresponding $G_m^n(r)$ given below

$$G_m^1(r) = \frac{\beta P}{\rho} - \frac{d}{r}A + \left[4\frac{d^2}{r^2} + \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^2 - \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^3\right]B, \quad r \geq d/2,$$
$$G_m^2(r) = \frac{\beta P}{\rho} - \frac{d}{r}A + \left[-m\frac{d^2}{r^2} + 4 - 4m\right]B, \quad r \geq d/2,$$
$$G_m^3(r) = \frac{\beta P}{\rho} - \frac{d}{r}A + \left[-m\frac{r}{d} + 1 + m\right]B, \quad r \geq d/2,$$
$$G_m^4(r) = \frac{\beta P}{\rho} - \frac{d}{r}A - \frac{d}{r}B\left[1-\frac{d}{r}\right]^{1/(2-m)}, \quad r \geq d/2,$$
$$G_m^5(r) = \frac{\beta P}{\rho} - \frac{d}{r}A\exp\left[-\frac{16}{35}\beta\epsilon\right] + \left[4\left(\frac{d}{r}\right)^2 + \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^2 - \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^3\right]B\exp\left[-\frac{16}{35}\beta\epsilon\right].$$

Appendix C

The expressions for $G_m^n(r)$ $(n = 1, 2, \ldots, 5)$ are given below:

$$G(r) = G_m^1(r) = -\frac{1}{(-1+4\eta)} + \left[\frac{4\eta}{(-1+4\eta)} - \frac{d}{r}\right]A + \left[4\left(\frac{d}{r}\right)^2 + \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^2 - \frac{(1-m)}{\left[1-\frac{3}{4}m\right]}\left(\frac{d}{r}\right)^3 - \frac{16\eta}{(-1+4\eta)}\right]B, \quad r \geq d/2,$$
$$G(r) = G_m^2(r) = -\frac{1}{(-1+4\eta)} + \left[\frac{4\eta}{(-1+4\eta)} - \frac{d}{r}\right]A + \left[-m\frac{d^2}{r^2} + 4 - 4m + \frac{20\eta m}{(-1+4\eta)} - \frac{16\eta}{(-1+4\eta)}\right]B, \quad r \geq d/2,$$
$$G(r) = G_m^3(r) = -\frac{1}{(-1+4\eta)} + \left[\frac{4\eta}{(-1+4\eta)} - \frac{d}{r}\right]A + \left[-m\frac{r}{d} + 1 + m - \frac{4\eta}{(-1+4\eta)}\right]B, \quad r \geq d/2,$$

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

$$G(r) = G_m^5(r) = -\frac{1}{(-1+4\eta)} + \left[\frac{4\eta \exp[-\frac{16}{35}\beta\epsilon]}{(-1+4\eta)} - \frac{d}{r}\exp\left[-\frac{16}{35}\beta\epsilon\left(\frac{r}{d}\right)^3\right]\right] A$$
$$+ \left[\left(\frac{d^3}{r^3} - \frac{d^2}{r^2}\right)\frac{\exp[-\frac{16}{35}\beta\epsilon\,(r/d)^3](m-1)}{[1-\frac{3}{4}m]} - \frac{16\eta\exp[-\frac{16}{35}\beta\epsilon]}{(-1+4\eta)} + \frac{4d^2}{r^2}\exp\left[-\frac{16}{35}\beta\epsilon\left(\frac{r}{d}\right)^3\right]\right] B, \quad r \geq d/2.$$

Appendix D

The expressions for $A\,\mathrm{sol}(0)_m^n$, $A\,\mathrm{sol}(1)_m^n$, $B\,\mathrm{sol}(0)_m^n$, and $B\,\mathrm{sol}(1)_m^n$, $(n = 1, 2, \ldots, 5)$ are given below.

$$A\,\mathrm{sol}(0)_m^1 = \frac{(3/2)\eta(-1-4\eta+3m\eta)}{(\eta-1)^2(m\eta-1)}, \quad A\,\mathrm{sol}(1)_m^1 = \frac{(4/3)(\alpha^6-3)(m-2)(-1+4\eta)\beta\epsilon\alpha^6}{(m\eta-1)},$$
$$B\,\mathrm{sol}(0)_m^1 = \frac{(3/16)\eta^2(-4+3m)}{(\eta-1)^2(m\eta-1)}, \quad B\,\mathrm{sol}(1)_m^1 = \frac{(1/12)(\alpha^6-3)(-4+3m)(-1+4\eta)\beta\epsilon\alpha^6}{(m\eta-1)},$$
$$A\,\mathrm{sol}(0)_m^2 = -\frac{(3/2)\eta(m\eta+1)}{(\eta-1)^2(m\eta-1)}, \quad A\,\mathrm{sol}(1)_m^2 = -\frac{(4/3)(-3+\alpha^6)(-1+4\eta)\beta\epsilon\alpha^6 m}{(m\eta-1)},$$
$$B\,\mathrm{sol}(0)_m^2 = \frac{(3/4)\eta^2}{(\eta-1)^2(m\eta-1)}, \quad B\,\mathrm{sol}(1)_m^2 = \frac{(1/3)\alpha^6\beta\epsilon(-3+\alpha^6)(-1+4\eta)}{(m\eta-1)},$$
$$A\,\mathrm{sol}(0)_m^3 = \frac{(3/4)\eta(-2+3m\eta)}{(\eta-1)^2(m\eta-1)}, \quad A\,\mathrm{sol}(1)_m^3 = \frac{(1/3)(-3+\alpha^6)(-1+4\eta)\beta\epsilon\alpha^6 m}{(m\eta-1)},$$
$$B\,\mathrm{sol}(0)_m^3 = \frac{3\eta^2}{((\eta-1)^2(m\eta-1))}, \quad B\,\mathrm{sol}(1)_m^3 = \frac{(4/3)\alpha^6\beta\epsilon(-3+\alpha^6)(-1+4\eta)}{(m\eta-1)},$$
$$A\,\mathrm{sol}(0)_m^4 = \frac{(3/4)\eta(-2-4\eta+3\eta m)}{(\eta-1)^2(m\eta-1)}, \quad A\,\mathrm{sol}(1)_m^4 = \frac{(1/3)(-3+\alpha^6)(-4+m)(-1+4\eta)\beta\epsilon\alpha^6}{(m\eta-1)},$$
$$B\,\mathrm{sol}(0)_m^4 = -\frac{(3/4)\eta^2(-2+m)(-1)^{1/(-2+m)}}{(\eta-1)^2(m\eta-1)},$$
$$B\,\mathrm{sol}(1)_m^4 = -\frac{(1/3)(-1)^{1/(-2+m)}(-3+\alpha^6)(-2+m)(-1+4\eta)\beta\epsilon\alpha^6}{(m\eta-1)},$$
$$A\,\mathrm{sol}(0)_m^5 = -\frac{(3/2)\eta(8\eta-6m\eta+1-4\eta+3\eta m)}{(\eta-1)^2(m\eta-1)},$$
$$A\,\mathrm{sol}(1)_m^5 = \frac{(4/3)\exp[\frac{2}{35}\beta\epsilon](-3+\alpha^6)(-9\beta\epsilon-70+35m+6\beta\epsilon m)(-1+4\eta)\beta\epsilon\alpha^6}{[35\eta\exp[-\frac{2}{5}\beta\epsilon]m+140\eta-140\eta\exp[-\frac{2}{5}\beta\epsilon]+6\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon]m-12\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon]-35]},$$
$$B\,\mathrm{sol}(0)_m^5 = \frac{(3/16)\eta^2(-4+3m)}{(\eta-1)^2(m\eta-1)},$$
$$B\,\mathrm{sol}(1)_m^5 = \frac{(1/12)\exp[\frac{2}{35}\beta\epsilon](-3+\alpha^6)(35+6\beta\epsilon)(-4+3m)(-1+4\eta)\beta\epsilon\alpha^6}{[35\eta\exp[-\frac{2}{5}\beta\epsilon]m+140\eta-140\eta\exp[-\frac{2}{5}\beta\epsilon]+6\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon]m-12\beta\epsilon\eta\exp[-\frac{2}{5}\beta\epsilon]-35]}.$$

Appendix E

The expressions for a_0, a_1, a_2, b_0 and b_1 are given below.

$$a_2 = \left\{70\exp\left[-\frac{16}{35}\beta\epsilon\right] - 12\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right] + 6\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right]m + 35\exp\left[-\frac{2}{35}\beta\epsilon\right] - 70\exp\left[-\frac{16}{35}\beta\epsilon\right]m\right\},$$
$$a_1 = \left\{-70\exp\left[-\frac{2}{35}\beta\epsilon\right] - 6\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right]m + 140\exp\left[-\frac{16}{35}\beta\epsilon\right]\right.$$
$$\left. +12\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right] - 35\exp\left[-\frac{16}{35}\beta\epsilon\right]m\right\},$$
$$a_0 = 35\exp\left[-\frac{2}{35}\beta\epsilon\right], \quad b_0 = 35\exp\left[-\frac{2}{35}\beta\epsilon\right],$$

$$b_1 = \left\{35\exp\left[-\frac{16}{35}\beta\epsilon\right]m + 140\exp\left[-\frac{2}{35}\beta\epsilon\right] - 140\exp\left[-\frac{16}{35}\beta\epsilon\right] + 6\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right]m - 12\beta\epsilon\exp\left[-\frac{16}{35}\beta\epsilon\right]\right\}$$

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